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OPERATION, MAINTENANCE AND MONITORING PLAN

VOLUME II - QUALITY ASSURANCE PROJECT PLAN

Summit National Superfund Site
Deerfield Township of Portage County, Ohio

QUALITY ASSURANCE PROJECT PLAN
OPERATION, MAINTENANCE AND MONITORING PLAN

Summit National Superfund Site
Deerfield Township of Portage County, Ohio

JULY 1994

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CONESTOGA-ROVERS & ASSOCIATES

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QUALITY ASSURANCE PROJECT PLAN (QAPP)

PROJECT TITLE: Summit National Superfund Site
Operation, Maintenance and Monitoring Plan

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LIST OF ACRONYMS AND SHORT FORMS

BNA	-	Base-Neutral and Acid Extractable Compounds
°C	-	Degree Centigrade
CRA	-	Conestoga-Rovers & Associates
DQO	-	Data Quality Objective
GC	-	Gas Chromatography
GC/MS	-	Gas Chromatography/Mass Spectrometry
IU	-	Intermediate Unit
MS/DUP	-	Matrix Spike/Laboratory Duplicate
MS/MSD	-	Matrix Spike/Matrix Spike Duplicate
NUS	-	Halliburton NUS Laboratory
OEPA	-	Ohio Environmental Protection Agency
PCB	-	Polychlorinated Biphenyls
PE	-	Performance Evaluation
PPL	-	Priority Pollutant List
QA	-	Quality Assurance
QA/QC	-	Quality Assurance/Quality Control
QAPP	-	Quality Assurance Project Plan
QAS	-	Quality Assurance Section
QC	-	Quality Control
RPD	-	Relative Percent Difference
RPM	-	Remedial Project Manager
Site	-	Summit National Superfund Site
SNFT	-	Summit National Facility Trust
SOP	-	Standard Operating Procedures
SVOC	-	Semi-Volatile Organic Compounds
SW-846	-	SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods", 3rd Edition, November 1986
TAL	-	Target Analyte List
TCL	-	Target Compound List
USEPA	-	United States Environmental Protection Agency
USU	-	Upper Sharon Unit
VOC	-	Volatile Organic Compounds
WTU	-	Water Table Unit

12.0 INTRODUCTION

The United States Environmental Protection Agency (USEPA) requires that all environmental monitoring and measurements efforts mandated or supported by USEPA participate in a centrally managed quality assurance (QA) program.

Any party generating data under this program has the responsibility to implement minimum procedures to assure that the precision, accuracy, completeness and representativeness of its data are known and documented. To ensure the responsibility is met uniformly, each party must prepare a written QA Project Plan (QAPP) covering each project it is to perform.

This QAPP presents the organization, objectives, functional activities and specific QA and Quality Control (QC) activities associated with the long term operation, maintenance and monitoring of the Summit National Superfund Site (Site) in Deerfield Township of Portage County, Ohio. This QAPP also describes the specific protocols which will be followed for sampling, sample handling and storage, chain-of-custody and laboratory and field analysis.

All QA/QC procedures will be in accordance with applicable professional technical standards, USEPA requirements, government regulations and guidelines and specific project goals and requirements. This QAPP has been prepared by Conestoga-Rovers & Associates (CRA) in accordance with all USEPA QAPP guidance documents in particular, Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans (QAMS-005/80), and the Region V Model QAPP (1991).

12.1 PROJECT DESCRIPTION

This QAPP has been developed for and is part of the long term Operation, Maintenance and Monitoring Plan (O&M Plan) for the Site. The project description is presented in Sections 1.0 and 2.0 of the O&M Plan.

The O&M Plan has been prepared pursuant to the requirements of the document "Statement of Work and Appendices to Statement of Work", Summit National Superfund Site, Deerfield Township of Portage County, Ohio printed on December 14, 1989 (Statement of Work).

The final effluent monitoring requirements presented in the QAPP have been prepared pursuant to the Substantive Permit for the Summit National Treatment Plant issued by the Ohio Environmental Protection Agency (OEPA) May 18, 1994 and discussions with OEPA and USEPA on May 19, 1994.

12.1.1 Site Background

A detailed Site background is presented in Section 1.0 of the O&M Plan.

12.1.2 Sampling Network and Rationale

The sampling network and rationale specified by the SOW is presented in Section 8.1 of the O&M Plan.

12.1.3 Project Objectives and Scope

The purpose of the O&M Plan is to provide operation, maintenance and monitoring guidelines for the Site during the period from completion of the remedial construction activities to termination of groundwater extraction, treatment and monitoring at the Site. This QAPP has been prepared in support of the O&M Plan to provide QA/QC procedures and requirements for the Consent Decree monitoring requirements specified in Section 8.1 of the O&M Plan to be performed during the long term operation, maintenance and monitoring of the Site. Specific objectives of the data collection activities include:

i) the annual collection and analysis of one surface water and sediment sample at the confluence of the south and east drainage ditches;

ii) the demonstration of hydraulic containment of Site-related contaminated groundwater in the Water Table Unit (WTU) and the Intermediate Unit (IU) by measurement and analysis of groundwater levels;

iii) the demonstration of reduction of the concentrations of Site-related contaminants in groundwater within the WTU and the IU to concentrations specified by the cleanup standards which are based on an individual 10^{-6} increased lifetime cancer risk for invididual compounds and a comulative non-carcinogence Hazard Index (HI) less than 1 or background, whichever occurs first by analysis of groundwater samples;

iv) the demonstration that the hydraulic and water quality characterization in groundwater within the Upper Sharon Unit (USU) is not significantly impacted by the Site by measurement and analysis of groundwater levels and by analysis of groundwater samples;

v) the demonstration that water quality characteristics in local residential wells are not impacted by the Site by analysis of well water samples; and

vi) the demonstration of the effectiveness of the groundwater treatment system by measuring influent and effluent flow rates, chemical analysis of the treated water effluent and chemical analysis of the emissions from the vapor phase carbon adsorption vents.

The evaluation of the data collected will determine if the groundwater collection and extraction system is performing to its design criteria, whether the contingency measures outlined in Section 8.1.2.5 of the O&M Plan require implementation and at what point in time operation of the WTU and IU extraction systems may be terminated. In addition, compliance with final effluent requirements of the groundwater treatment system will be evaluated by the data.

The Statement of Work required that the final effluent be monitored for the Priority Pollutant List of parameters. However, the Substantive Permit issued by OEPA required that different parameters be monitored. The parameters required to be monitored, as presented in Table 12.4, were from the Target Compound List and Target Analyte List and not the Priority Pollutant List. Consequently, the methods to be used for the analysis of the final effluent will be consistent with the methods to be used for the analysis of the groundwater. The OEPA discharge limits are presented in Table 12.4. Select metals discharge limits will be achieved by reporting to the laboratory's instrument detection limits and have been identified on the table with a footnote. The OEPA discharge limit for antimony cannot be achieved by the laboratory and the laboratory will report antimony to the instrument detection limit. This has been deemed acceptable by OEPA.

12.1.4 Parameters to be Tested and Frequency

Sample matrices, analytical parameters and frequencies of sample collection are presented in Table 12.1.

12.1.5 Data Quality Objectives (DQOs)

Data quality objectives (DQOs) are qualitative and quantitative statements which specify the quality of the data required to support decisions made during investigation activities and are based on the end uses of the data to be collected. As such, different data uses may require different levels of data quality. There are five analytical levels which address various data uses and the QA/QC effort and methods required to achieve the desired level of quality.

DQOs have been established in accordance with the USEPA guidance document entitled "Data Quality Objectives for Remedial Response Activities - Development Process", dated March 1987, in conjunction with the document, "Data Quality Objectives for Remedial Response Activities - Example Scenario RI/FS Activities at a Site with Contaminated Soils and Groundwater", dated March 1987. Reference to these documents ensures that the database developed during the Site activities meets the objectives and quality necessary for its intended use.

DQOs can be classified for the measurement data by defining the level of analytical support assigned to each type of data measurement.

The following defines the different levels of analytical support:

i) Level I - Field screening or analysis using portable instruments;

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSES PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
Groundwater Monitoring During Operation and Maintenance									
WTU, IU Groundwater (system startup to one year)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	44	5	5	3	57	3	171
WTU, IU Groundwater (Year 2 to Year 4)	water level pH SCOND temperature	SSPL [4]	44	5	5	3	57	2	114
WTU, IU Groundwater (Year 6 to Termination)	water level pH SCOND temperature	SSPL	44	5	5	3	57	1	57
USU Groundwater (System startup to one year)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	5	1	1	1	8	2	16
USU Groundwater (Year 2 to Year 4)	water level pH SCOND temperature	SSPL	5	1	1	1	8	1	8

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSES PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
USU Groundwater (Year 6 and every 2nd year to termination)	water level pH SCOND temperature	SSPL	5	1	1	1	8	once every 2 years	8 every 2 years
All Monitoring Wells Groundwater (Year 5 and every 5th year to termination)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	once every 5 years	62 every 5 years
Residential Well Groundwater (system startup to one year)	pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	3	1	1	1	6	2	12
Residential Well Groundwater (Year 2 and every 2nd year until one year after confirmation)	pH SCOND temperature	SSPL	3	1	1	1	6	once every 2 years	6 every 2 years
Sediment (at confluence of south and east drainage ditches)		TCL VOC TCL SVOC TCL Pesticides/PCB	1	0	1	1	3	1	3

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSES PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
Surface Water (at confluence of south and east drainage ditches)	pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB	1	1	1	1	4	1	4
<u>Treatment System Monitoring</u>									
Treatment Plant Effluent Water (Month 1)	Influent/Effluent Flow	OEPA VOC [5] OEPA BNA OEPA Metals	1	0	0	0	1	8	8
Treatment Plant Effluent Water (Months 2 to termination)	Influent/Effluent Flow	OEPA VOC OEPA BNA OEPA Metals	1	0	0	0	1	12	12
Treatment Plant Air Emissions (Startup to termination)	Influent/Effluent Flow	PPL [6] VOC/ TO-14 [7]	2	0	0	0	2	1	2

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSES PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
Termination Monitoring [8]									
All Monitoring Wells Groundwater (one year prior to termination)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	4	248
All Monitoring Wells Groundwater (monthly for the first three months once cleanup standards are achieved)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	3	186
All Monitoring Wells Groundwater (Years 1 and 2 post-termination of extraction system)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	2	124

TABLE 12.1

SUMMARY OF SAMPLING AND ANALYSES PROGRAM
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Sample Matrix	*Field Parameters* [2]	*Laboratory Parameters*	*Investigative Samples*	*QC Samples* [1] *Field Blanks*	*Field Duplicates*	*Matrix Spike MS/MSD* [3]	*Total Per Round*	*Frequency Per Year*	*Total Per Year*
All Monitoring Wells Groundwater (Year 3 through 5 post-termination of extraction system)	water level pH SCOND temperature	TCL VOC TCL SVOC TCL Pesticides/PCB TAL Inorganics	49	5	5	3	62	1	62

1 One trip blank sample will be shipped with each cooler of monitoring well samples collected for VOC analysis.
2 SCOND = Specific conductance
3 Matrix spike/matrix spike duplicate (MS/MSD) analyses are required for organic analyses. Samples designated for MS/MSD analyses will be collected at a frequency of one per group of twenty (20) or fewer investigative samples. For MS/MSD samples within a water matrix, triple the normal sample volumes will be collected for VOC, and double the normal volumes will be collected for extractable organics and PCB/pesticides. Inorganics analysis will require either MS/MSD or MS and a duplicate sample analysis.
4 A Site-specific parameter list will be developed and submitted to USEPA and OEPA for modification and/or approval at the end of the first year of operation.
5 OEPA = Ohio Environmental Protection Agency Final effluent monitoring requirements.
6 PPL = Priority pollutant list of analytes.
7 TO-14 = "The determination of volatile organic compounds (VOCs) in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analysis", USEPA Compedium Method TO-14.
8 Frequency of sampling may change based on the results of monitoring as specified in the Consent Decree.

ii) Level II - Field analyses using more sophisticated portable analytical instruments;

iii) Level III - All analyses performed in off-Site analytical laboratories using EPA procedures other than the Contract Laboratory Program (CLP) Routine Analytical Services (RAS);

iv) Level IV - CLP-RAS performed in a CLP analytical laboratory using CLP procedures; and

v) Level V - Non-standard analytical methods performed in an off-Site laboratory.

Table 12.2 presents the level of analytical support for each group of parameters.

12.1.6 Monitoring Schedule

The monitoring schedule is presented on Figure 8.1 of the O&M Plan.

TABLE 12.2

LEVELS OF DATA QUALITY OBJECTIVES (DQO) ANALYTICAL SUPPORT
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Matrix	*Analysis*	*Analytical Support*
Sediment	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
Surface Water	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
Groundwater (Quality Monitoring)	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
	TAL Inorganics	Level III
	Water Level	Level I
	pH	Level I
	Specific Conductance	Level I
Groundwater (Residential Wells)	TCL VOC	Level III
	TCL SVOC	Level III
	TCL Pesticides/PCBs	Level III
	TAL Inorganics	Level V
Effluent Water (Treatment System)	OEPA VOCs	Level III
	OEPA BNAs	Level III
	OPEA Metals	Level III
Air (Treatment System Emissions)	Priority Pollutant Volatile Organic Compounds	Level III

12.2 PROJECT ORGANIZATION AND RESPONSIBILITY

The organization for the key staff with QA/QC responsibilities is presented in Figure 12.1.

A summary of responsibilities of key personnel follows:

Gary Gifford - Trust Chairperson - SNFT (Summit National Facility Trust)

- general overview of the project to ensure that the PRPs objectives are met
- participation in key negotiations with the USEPA
- liaison with USEPA and OEPA
- managerial guidance to the Engineering Consultant's Project Manager
- approval of the QAPP

Jack Michels - Project Manager - CRA

- technical guidance to SNFT
- participation in key technical negotiations with USEPA and SNFT
- liaison with USEPA and OEPA
- approval of the QAPP

Steven Day - QA/QC Officer - Analytical and Field Activities - CRA

- systems audits - laboratory activities
- overview and review field QA/QC
- coordinate supply of performance evaluation samples
- review laboratory QA/QC
- data validation and assessment
- advise on data corrective action procedures
- preparation and review of RD activities reports
- QA/QC representation of project activities
- management of field activities and field QA/QC
- data assessment
- preparation and review of RD activities report
- technical representation of field activities
- preparation of standard operating procedures (SOPs) for field activities
- approval of the QAPP

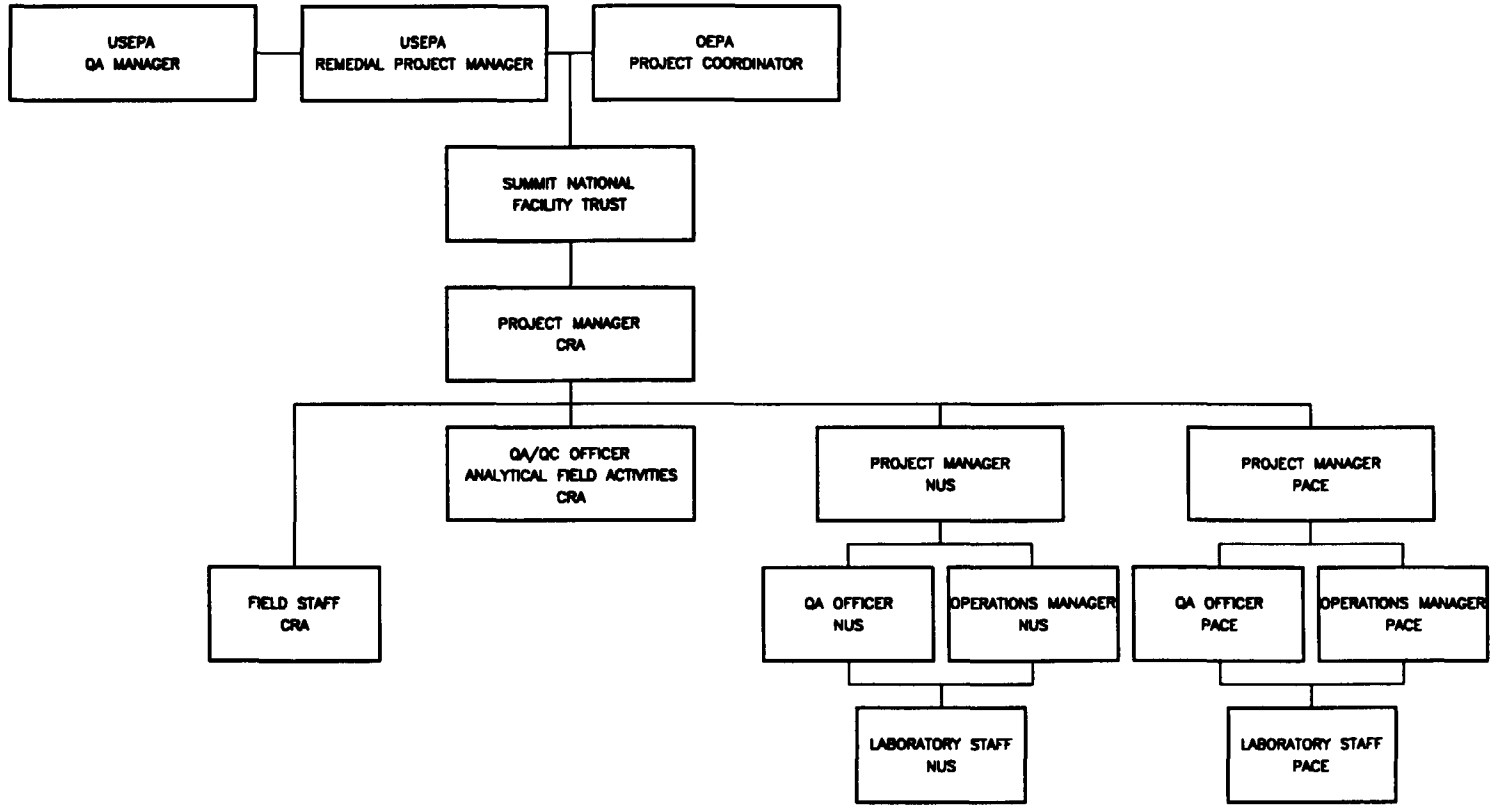

figure 12.1
QA/QC ORGANIZATION
SUMMIT NATIONAL SUPERFUND SITE
Deerfield Township Of Portage County, Ohio

CRA

Halliburton NUS Laboratory (NUS)
5350 Cambells Run Road
Pittsburg, Pennsylvania 15205
(412) 747-2500

- as analytical subcontractor to the Summit National Facility Trust (SNFT), will perform the majority of the chemical analyses of samples collected during the activities.

James Lieb - Project Manager - NUS

- ensures all resources of the laboratory are available on an as-required basis
- overview of final analytical reports
- approval of the QAPP

Chuck Kieda - Operations Manager - NUS

- coordinate laboratory analyses
- supervise in-house chain-of-custody
- schedule sample analyses
- oversee data review
- oversee preparation of analytical reports
- approve final analytical reports prior to submission to the Engineering Consultant

Lisa Manning - QA Officer - NUS

- overview laboratory quality assurance
- overview QA/QC documentation
- conduct detailed data review
- decide laboratory corrective actions, if required
- technical representation of laboratory QA procedures
- preparation of laboratory SOPs
- approval of the QAPP

Terri Wynnik - Sample Custodian - NUS

- receive and inspect the incoming sample containers
- record the condition of the incoming sample containers
- sign appropriate documents
- verify chain of custody and its correctness
- notify Project manager of sample receipt and inspection
- assign a unique identification number and customer number and enter each into the sample receiving log
- with the help of the operations manager, initiate transfer of the samples to appropriate lab sections
- control and monitor access/storage of samples and extracts

Pace, Incorporated (Pace)
1710 Douglas Drive North
Minneapolis, Minnesota 55422
(612) 544-5543

- as subcontractor to NUS will perform the analysis of VOC in air using method TO-14

Liesa Shanahan - Project Manager - Pace

- ensures all resources of the laboratory are available on an as-required basis
- overview of final analytical reports
- approval of the QAPP

Liesa Shanahan - Operations Manager - Pace

- coordinate laboratory analyses
- supervise in-house chain-of-custody
- schedule sample analyses
- oversee data review
- oversee preparation of analytical reports
- approve final analytical reports prior to submission to the Engineering Consultant

Joe Novotny - QA Officer - Pace

- overview laboratory quality assurance
- overview QA/QC documentation
- conduct detailed data review
- decide laboratory corrective actions, if required
- technical representation of laboratory QA procedures
- preparation of laboratory SOPs
- approval of the QAPP

Paul Ernst - Sample Custodian - Pace

- receive and inspect the incoming sample containers
- record the condition of the incoming sample containers
- sign appropriate documents
- verify chain of custody and its correctness
- notify Project manager of sample receipt and inspection
- assign a unique identification number and customer number and enter each into the sample receiving log
- with the help of the operations manager, initiate transfer of the samples to appropriate lab sections
- control and monitor access/storage of samples and extracts

Primary responsibility for project quality rests with CRA's QA/QC Officer - Analytical and Field Activities. Ultimate responsibility for project quality rests with CRA's Project Manager. Independent quality assurance will be provided by the Laboratory Project Manager and QA Officer prior to release of all data to the contractor.

USEPA RESPONSIBILITIES

The USEPA Region V Remedial Project Manager (RPM) will be responsible for the overview of this project. The RPM will also be responsible for providing approval of the QAPP. Anthony Rutter is the RPM for the Remedial Action activities.

The Laboratory Scientific Support Section of the Central Regional Laboratory of USEPA Region V or USEPA Central District Office will be responsible for performance and system audits of the laboratory analyses and field activities. Performance evaluation (PE) audits will be ordered at the discretion of the USEPA.

Additionally, the USEPA Region V Quality Assurance Manager is responsible for reviewing and for providing final approval of the QAPP. Willie H. Harris is Region V QA Manager.

12.3 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analyses and reporting that will provide results which are legally defensible in a court of law. Specific procedures for sampling, chain-of-custody, laboratory instruments calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of field equipment and corrective action are described in other section of this QAPP. The purpose of this section is to address the specific objectives for accuracy, precision, completeness, representativeness and comparability.

12.3.1 Level of QC Effort

To assess the quality of data resulting from the field sampling program, field duplicate samples, field blank samples (bailer rinse), trip blank samples, preservative blank samples and matrix spike samples will be taken and submitted to the analytical laboratory.

Field duplicate samples will be collected at a frequency of one per ten or fewer investigative samples per parameter set for all sample matrices, with a minimum of one field duplicate sample submitted per sampling event. Matrix spike and matrix spike duplicate (MS/MSD) samples will be analyzed at a minimum frequency of one per 20 or fewer samples for each organic analysis. For the metals analyses, one matrix spike and laboratory duplicate (MS/DUP) or MS/MSD will be analyzed at a minimum frequency of one per 20 or fewer investigative samples.

Field blank samples will be submitted at a frequency of one per ten well purging/sampling equipment cleanings or a least once per day of well purging/sampling equipment cleanings, whichever is more

frequent. Field blank samples will be collected by routing deionized water through decontaminated sampling equipment. Field blank samples will be analyzed to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination.

Preserved trip blank samples for VOC analyses (prepared by the laboratory and consisting of organic-free water poured into the sample vials) will be shipped with each shipping container of VOC sample vials by the laboratory. Trip blank samples will be handled in a manner consistent with actual field sample handling and will be shipped back to the laboratory with the monitoring well samples. The trip blanks will provide a measure of potential cross contamination of samples during shipment and handling. However, it should be noted that trip blanks will not be opened in the field.

Upon examination of the results obtained by the laboratory, if any of the aforementioned blanks are found to contain any of the target analytes, the following procedure will be followed. First, determine if the contamination is real by examining the associated investigative samples and method blanks. If the contamination can be traced to an isolated source, e.g. a highly contaminated sample, the data is to remain unqualified. Otherwise, the data will be examined to determine the extent of contamination and all associated data will be qualified according to the data validation guidelines given in Section 12.9.

Field duplicate samples will be analyzed to check for sampling and analytical reproducibility. Field duplicate samples will be used as a measure of precision throughout the sampling event. Comparison of field duplicate samples will be based upon the target analytes, both non-detected and detected, and the relative percent differences (RPD) of each analyte's concentrations. The parameters which do not meet the criteria may only be used as qualitative measurements. Professional judgment shall determine the RPD limits on a sample-to-sample basis.

The level of QC effort provided by the laboratory for analysis of the samples will be equivalent to the level of QC effort specified in the standard operating procedures (SOPs) in Appendix 12.1.

The level of QC effort for the field measurements of pH and specific conductance will be as described in the SOPs in Appendix 12.1. Temperature readings will be obtained with pH measurements. Water level measurements will be to the nearest 0.01 ft. using an electric sounding water level meter.

12.3.2 Accuracy, Precision and Sensitivity of Analyses

The fundamental QA objective with respect to accuracy and precision of laboratory analytical data is to achieve the QC acceptance criteria of the analytical protocols. The sensitivities required for the analyses will be at least the targeted quantitation limits in Tables 12.3 through 12.6. It should be noted that the quantitation limits listed are targeted quantitation limits. Actual sample quantitation limits are highly matrix dependent.

SOPs for laboratory analyses are provided in Appendix 12.1. These include the required accuracy, precision, sensitivity of the analyses. SOPs for the field equipment to measure pH, conductivity and temperature are also provided in Appendix 12.1.

12.3.3 Completeness, Representativeness and Comparability

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. It is expected that the

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	
	Water (µg/L)	*Low Soil/Sediment* (µg/kg)
Volatile Organic Compounds		
acetone	50	50
benzene	5	5
bromodichloromethane	5	5
bromoform	5	5
bromomethane	10	10
butanone	50	50
carbon disulfide	5	5
carbon tetrachloride	5	5
chlorobenzene	5	5
chloroethane	10	10
chloroform	5	5
chloromethane	10	10
cis-1,3-dichloropropene	5	5
dibromochloromethane	5	5
1,1-dichloroethane	5	5
1,2-dichloroethane	5	5
1,1-dichloroethene	5	5
1,2-dichloroethene (total)	5	5
1,2-dichloropropane	5	5
ethylbenzene	5	5
2-hexanone	50	50
methylene chloride	5	5
4-methyl-2-pentanone	50	50
styrene	5	5
1,1,2,2-tetrachloroethane	10	10
tetrachloroethene	5	5
toluene	5	5
trans-1,3-dichloropropene	5	5
1,1,1-trichloroethane	5	5
1,1,2-trichloroethane	5	5
trichloroethene	5	5
vinyl chloride	10	10
xylenes (total)	5	5

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	
	Water (µg/L)	*Low Soil/Sediment (µg/kg)*
Semi-Volatile Organic Compounds		
acenaphthene	10	330
acenaphthylene	10	330
anthracene	10	330
benzo(a)anthracene	10	330
benzo(a)pyrene	10	330
benzo(b)fluoranthene	10	330
benzo(g,h,i)perylene	10	330
benzo(k)fluoranthene	10	330
bis(2-chloroethoxy)methane	10	330
bis(2-chloroethyl)ether	10	330
2,2'-oxybis(1-chloropropane)	10	330
bis(2-ethylhexyl)phthalate	10	330
butylbenzylphthalate	10	330
4-bromophenylphenyl ether	10	330
carbazole	10	330
4-chloroaniline	10	330
2-chloronaphthalene	10	330
4-chlorophenyl phenyl ether	10	330
chrysene	10	330
dibenz(a,h)anthracene	10	330
dibenzofuran	10	330
1,2-dichlorobenzene	10	330
1,3-dichlorobenzene	10	330
1,4-dichlorobenzene	10	330
3,3'-dichlorobenzidine	50	660
diethylphthalate	10	330
dimethylphthalate	10	330
di-n-butyphthalate	10	330
di-n-octylphthalate	10	330
2,4-dinitrotoluene	10	330
2,6-dinitrotoluene	10	330
fluoranthene	10	330
fluorene	10	330
hexachlorobenzene	10	330
hexachlorobutadiene	10	330
hexachlorocyclopentadiene	10	330
hexachloroethane	10	330
indeno(1,2,3-cd)pyrene	10	330
isophorone	10	330
2-methylnaphthalene	10	330

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	
	Water (µg/L)	*Low Soil/Sediment (µg/kg)*
Semi-Volatile Organic Compounds (Con't)		
naphthalene	10	330
2-nitroaniline	50	1,600
3-nitroaniline	50	1,600
4-nitroaniline	50	1,600
nitrobenzene	10	330
N-nitroso-di-n-propylamine	10	330
N-nitrosodiphenylamine (diphenylamine)	10	330
phenanthrene	10	330
pyrene	10	330
1,2,4-trichlorobenzene	10	330
4-chloro-3-methylphenol	10	330
2-chlorophenol	10	330
2,4-dichorophenol	10	330
2,4-dimethylphenol	10	330
2,4-dinitrophenol	50	1,600
4,6-dinitro-2-methylphenol	50	1,600
2-methylphenol	10	330
4-methylphenol	10	330
2-nitrophenol	10	330
4-nitrophenol	50	1,600
pentachlorophenol	50	1,600
phenol	10	330
2,4,5-trichlorophenol	10	330
2,4,6-trichlorophenol	10	330

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	
	Water (µg/L)	*Low Soil/Sediment* (µg/kg)
Pesticides		
aldrin	0.05	8
alpha-BHC	0.05	8
beta-BHC	0.05	8
alpha-chlordane	0.5	8
gamma-chlordane	0.5	8
4,4'-DDD	0.1	16
4,4'-DDE	0.1	16
4,4'-DDT	0.1	16
delta-BHC	0.05	16
dieldrin	0.1	16
endosulfan I	0.05	8
endosulfan II	0.1	16
endosulfan sulfate	0.1	16
endrin	0.1	16
endrin ketone	0.1	16
gamma-BHC (Lindane)	0.05	8
heptachlor	0.05	8
heptachlor epoxide	0.05	8
methoxychlor	0.5	8
toxaphene	1.0	160
PCBs		
aroclor 1016	0.5	80
aroclor 1221	0.5	80
aroclor 1232	0.5	80
aroclor 1242	0.5	80
aroclor 1248	0.5	80
aroclor 1254	1.0	160
aroclor 1260	1.0	160

TABLE 12.3

TARGETED QUANTITATION LIMITS FOR TCL/TAL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	
	Water (µg/L)	*Low Soil/Sediment (µg/kg)*
Inorganics		
aluminum	200	40
antimony	60	12
arsenic	10	2
barium	200	40
beryllium	5	1
cadmium	5	1
calcium	5,000	1,000
chromium	10	2
cobalt	50	10
copper	25	5
iron	100	20
lead	3	0.6
magnesium	5,000	1,000
manganese	15	3
mercury	0.2	0.1
nickel	40	8
potassium	5,000	1,000
selenium	5	1
silver	10	2
sodium	5,000	1,000
thallium	10	2
vanadium	50	10
zinc	20	4
cyanide	10	1

[1] Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

TABLE 12.4

TARGETED QUANTITATION LIMITS FOR FINAL EFFLUENT ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	*OEPA Discharge Limits*
	Water (µg/L)	*Water (µg/L)*
Volatile Organic Compounds		
acetone	10	927
benzene	5	7
1,1-dichloroethane	5	7
1,2-dichloroethane	5	21
1,1-dichloroethene	5	5
1,2-dichloroethene (total)	5	26
ethylbenzene	5	5
methylene chloride	5	5
methyl ethyl ketone (2-butanone)	10	442
methyl isobutyl ketone (4-methyl-2-pentanone)	10	15
toluene	5	5
1,1,1-trichloroethane	5	12
trichloroethene	5	5
xylenes (total)	5	6
Base/Neutral Compounds		
bis(2-ethylhexyl)phthalate	10	10
isophorone	10	10
2-methylnapthalene	10	10
naphthalene	10	10
Acid Compounds		
4-chloro-3-methylphenol (p-chloro-m-aresol)	10	10
phenol	10	10
2-methylphenol	10	10
4-methylphenol	10	10

TABLE 12.4

TARGETED QUANTITATION LIMITS FOR FINAL EFFLUENT ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]	*OEPA Discharge Limits*
	Water (µg/L)	*Water (µg/L)*
Metals		
antimony [2]	7	5
arsenic	3	7
iron	20	300
aluminum	50	536
barium	5	219
calcium	100	201,785
chromium (total)	10	5
cobalt	10	14
copper [2]	1	2
lead [2]	1	1
magnesium	50	72,151
manganese (dissolved)	5	6,818
nickel (dissolved)	20	14
potassium	200	6,415
zinc	10	188

[1] Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

[2] Targeted quantitation limit is the instrument detection limit.

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water ($\mu g/L$)
Volatile Organic Compounds	
acetone	5
benzene	1
bromodichloromethane	1
bromoform	1
bromomethane	1
2-butanone	5
carbon disulfide	1
carbon tetrachloride	1
chlorobenzene	1
chloroethane	1
chloroform	1
chloromethane	1
cis-1,3-dichloropropene	1
dibromochloromethane	1
1,1-dichloroethane	1
1,2-dichloroethane	1
1,1-dichloroethene	1
1,2-dichloroethene (total)	1
1,2-dichloropropane	1
ethylbenzene	1
2-hexanone	5
methylene chloride	2
4-methyl-2-pentanone	5
styrene	1
1,1,2,2-tetrachloroethane	1
tetrachloroethene	1
toluene	1
trans-1,3-dichloropropene	1
1,1,1-trichloroethane	1
1,1,2-trichloroethane	1
trichloroethene	1
vinyl chloride	1
xylenes (total)	1

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water (µg/L)
Semi-Volatile Organic Compounds	
acenaphthene	5
acenaphthylene	5
anthracene	5
benzo(a)anthracene	5
benzo(a)pyrene	5
benzo(b)fluoranthene	5
benzo(g,h,i)perylene	5
benzo(k)fluoranthene	5
benzyl alcohol	50
bis(2-chloroethoxy)methane	5
2,2'-oxybis(1-chloropropane)	5
bis(2-chloroisopropyl)ether	5
bis(2-ethylhexyl)phthalate	5
butyl benzyl phthalate	5
4-bromophenylphenyl ether	5
4-chloroaniline	5
2-chloronaphthalene	5
4-chlorophenyl phenyl ether	5
chrysene	5
dibenz(a,h)anthracene	5
dibenzofuran	5
1,2-dichlorobenzene	5
1,3-dichlorobenzene	5
1,4-dichlorobenzene	5
3,3'-dichlorobenzidine	20
diethylphthalate	5
dimethylphthalate	20
di-n-butyphthalate	5
di-n-octylphthalate	5
2,4-dinitrotoluene	5
2,6-dinitrotoluene	5
fluoranthene	5
fluorene	5
hexachlorobenzene	5
hexachlorobutadiene	5

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1] *Water (µg/L)*
Semi-Volatile Organic Compounds (continued)	
hexachlorocyclopentadiene	5
hexachloroethane	5
indeno(1,2,3-cd)pyrene	5
isophorone	5
2-methylnaphthalene	5
naphthalene	5
2-nitroaniline	20
3-nitroaniline	20
4-nitroaniline	20
nitrobenzene	5
N-nitroso-di-n-propylamine	5
N-nitrosodiphenylamine (diphenylamine)	5
phenanthrene	5
pyrene	5
1,2,4-trichlorobenzene	5
benzoic acid	50
4-chloro-3-methylphenol	5
2-chlorophenol	5
2,4-dichorophenol	5
2,4-dimethylphenol	5
2,4-dinitrophenol	20
4,6-dinitro-2-methylphenol	20
2-methylphenol	5
4-methylphenol	5
2-nitrophenol	5
4-nitrophenol	20
pentachlorophenol	20
phenol	5
2,4,5-trichlorophenol	20
2,4,6-trichlorophenol	5

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water ($\mu g/L$)
Pesticides	
aldrin	0.01
alpha-BHC	0.01
beta-BHC	0.01
alpha-chlordane	0.01
gamma-chlordane	0.01
4,4'-DDD	0.01
4,4'-DDE	0.02
4,4'-DDT	0.02
delta-BHC	0.01
dieldrin	0.02
endosulfan I	0.01
endosulfan II	0.02
endosulfan sulfate	0.02
endrin	0.02
endrin ketone	0.02
gamma-BHC (Lindane)	0.01
heptachlor	0.01
heptachlor epoxide	0.01
methoxychlor	0.1
toxaphene	1.0
PCBs	
Aroclor 1016	0.20
Aroclor 1232	0.40
Aroclor 1242	0.20
Aroclor 1248	0.20
Aroclor 1254	0.20
Aroclor 1260	0.20

TABLE 12.5

TARGETED QUANTITATION LIMITS FOR RESIDENTIAL WELL ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1]
	Water (µg/L)
Inorganics	
Aluminum	100
Antimony	5
Arsenic	2
Barium	20
Beryllium	1
Cadmium	1
Calcium	500
Chromium	10
Cobalt	10
Copper	10
Iron	100
Lead	2
Magnesium	500
Manganese	10
Mercury	0.2
Nickel	20
Potassium	750
Selenium	3
Silver	10
Sodium	500
Thallium	10
Vanadium	10
Zinc	20
Cyanide	10

1 Actual sample quantitation limits are highly matrix and dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

TABLE 12.6

TARGETED QUANTITATION LIMITS FOR AIR ANALYSES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

	Targeted Quantitation Limits [1] *Air (ppbv)*
Volatile Organic Compounds	
benzene	3.10
bromomethane	2.50
carbon tetrachloride	1.60
chlorobenzene	3.00
chloroethane	3.70
chloroform	2.00
chloromethane	4.80
1,3-dichloropropene	3.30
1,1-dichloroethane	6.00
1,2-dichloroethane	2.40
1,1-dichloroethene	2.50
1,2-dichloroethene	4.60
1,2-dichloropropane	2.10
ethylbenzene	2.70
methylene chloride	5.30
1,1,2,2-tetrachloroethane	1.80
tetrachloroethene	2.10
toluene	3.40
1,1,1-trichloroethane	1.80
1,1,2-trichloroethane	2.60
trichloroethene	1.80
vinyl chloride	3.90

[1] Actual sample quantitation limits are highly matrix and laboratory dependant and are not always achievable. Targeted quantitation limits presented are for guidance only and may not be achievable.

[2] ppbv = parts per billion by volume

project laboratory will provide data meeting the QC acceptance criteria for 90 percent or more for all samples tested using the referenced methods. Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness (\%)} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition or an environmental condition. Representativeness is a qualitative parameter which is dependent upon the proper design of the sampling program and proper laboratory protocol. The sampling network was designed to provide data representative of Site conditions. During development of this network, consideration was given to the historical Site operations, existing analytical data and physical setting and processes. The rationale of the sampling network is discussed in detail in the O&M Plan. Representativeness will be satisfied by insuring that the O&M Plan is followed, proper sampling techniques are used, proper analytical procedures are followed and holding times of the samples are not exceeded in the laboratory. Representativeness will be assessed by field duplicate sample data.

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of sampling and analytical methods. The procedures used to obtain the planned analytical data, as documented in the QAPP, are expected to provide comparable data. These new analytical data, however, may not be directly comparable to existing data because of difference in procedures and QA objectives.

12.3.4 Field Measurements

Measurement data will be generated in many field activities. These activities include, but are not limited to, the following:

i) documenting time and weather conditions;
ii) determining pH, specific conductivity, and temperature of groundwater samples; and
iii) verifying pre-sampling purge volumes.

The general QA objective for such measurement data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the SOPs in Appendix 12.1.

12.4 SAMPLING PROCEDURES

The following subsections present the sampling procedures for the various media at the Site.

12.4.1 Equipment Cleaning

All sampling equipment which may come in contact with potentially contaminated materials shall be decontaminated prior to field use and after each sample is collected to prevent cross-contamination of the samples. Duplicate samples shall be collected concurrently with original samples, therefore, sampling equipment will not be decontaminated before collection of the duplicate. Decontamination of equipment will be performed as follows:

i) clean water and non-phosphate detergent wash using a brush, if necessary, to remove all visible foreign matter;
ii) rinse thoroughly with potable water;
iii) rinse with isopropyl alcohol;
iv) rinse thoroughly with deionized water; and
v) allow the equipment to air dry on a clean plastic sheet as long as possible.

Following final rinse, openings will be visually inspected to verify they are free of soil particulates and other solid material which may contribute to possible sample cross-contamination.

Fluids used for cleaning will not be recycled. All wash water, rinse water and decontamination fluids will be treated in the on-Site treatment system.

12.4.2 Field Sampling

12.4.2.1 Sample Labeling

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. The sample numbering system to be used is described as follows:

Example: GW-010194-XX-001

GW	- designates types of sample (GW-groundwater, SW-surface water, SD-sediment, RW-residential well, A-air)
010194	- designates date of collection presented as month/day/year
XX	- sampler's initials
001	- sequential number starting with 001 at the start of the project

Field QC samples will also be numbered with a unique sample number, consistent with the numbering system described above to prevent laboratory bias of field QC samples.

12.4.2.2 Field Log

The field logbook will be a bound document with consecutively numbered pages. The entries for each day will commence on a new page which will be dated. All entries will be made using waterproof ink. Corrections will be made by marking through the error with a single line, so as to remain legible, and initialing this action followed by writing the correction.

The following information will be recorded in the field logbook for each sample collected:

i) site location identification;
ii) unique sample identification number;
iii) date and time (in military time format) of sample collection;
iv) weather conditions;
v) designation as to the type of sample (groundwater, soil, etc.);
vi) designation as to the means of collection (grab, bailer, etc.);
vii) sample depth (where appropriate)
viii) name of sampler;
ix) analyses to be performed on sample;
x) volume and number of sample containers; and
xi) any other relevant comments such as odor, staining, texture, filtering, preservation, etc.

12.4.2.3 Chain-Of-Custody Forms

Chain-of-custody records will be used to track all samples from time of sampling to the arrival of samples at the laboratory.

Each sample container being shipped to the laboratory will contain a chain-of-custody form. The chain-of-custody form consists of four copies which are distributed to the sampler, to the shipper, to the contract laboratory and to the office file of CRA. The sampler and shipper will maintain their copies while the other two copies are enclosed in a waterproof enclosure within the shipping container. The laboratory, upon receiving the samples, will complete the remaining copies. The laboratory will maintain one copy for its records. The executed original will be returned to CRA with the data deliverables package. A typical chain-of-custody form is presented on Figure 12.2.

CRA
CONESTOGA-ROVERS & ASSOCIATES
10400 West Higgins Road - Suite 103
Rosemont, IL 60018 (708)299-9933

SHIPPED TO (Laboratory Name):

REFERENCE NUMBER:

PROJECT NAME:

CHAIN OF CUSTODY RECORD

SAMPLER'S SIGNATURE: _____ PRINTED NAME: _____

SEQ. No.	DATE	TIME	SAMPLE No.	SAMPLE MATRIX	No. OF CONTAINERS	PARAMETERS	REMARKS
			TOTAL NUMBER OF CONTAINERS				

SAMPLE

RELINQUISHED BY: ①	DATE: TIME:	RECEIVED BY: ②	DATE: TIME:
RELINQUISHED BY: ②	DATE: TIME:	RECEIVED BY: ③	DATE: TIME:
RELINQUISHED BY: ③	DATE: TIME:	RECEIVED BY: ④	DATE: TIME:

METHOD OF SHIPMENT: AIR BILL No.

White -Fully Executed Copy
Yellow -Receiving Laboratory Copy
Pink -Shipper Copy
Goldenrod -Sampler Copy

SAMPLE TEAM:

RECEIVED FOR LABORATORY BY:

DATE: TIME:

figure 12.2

TYPICAL CHAIN-OF-CUSTODY RECORD
SUMMIT NATIONAL SUPERFUND SITE
Deerfield Township Of Portage County, Ohio

12.4.2.4 Sample Containers and Handling

Required sample containers, sample preservation methods, maximum holding times and filling instructions are provided in Table 12.7.

All samples will be placed in appropriate sample containers, labeled and properly sealed. The sample labels will include sample number, place of collection, date and time of collection and analyses to be performed. Samples will be cushioned within the shipping coolers by the use of vermiculite, foam chips and/or bubble pack. Samples will be kept cool by the use of sealed plastic bags of ice or cooler packs. A trip blank will accompany each shipment of multiple investigative groundwater samples submitted for VOC analysis.

Samples will be shipped by commercial courier or will be hand delivered on a daily basis to the project laboratory. The exception to this will be samples which are collected on a Sunday or holiday. For samples collected on a Sunday or holiday, additional ice will be placed in the coolers, the coolers will be sealed and kept in a designated secure area until they are picked up by the courier, or hand delivered to the laboratory, on the next business day.

Two seals comprised of chain-of-custody tape will be placed over the lid on the front right and back left of each shipping cooler prior to shipment to secure the lid and provide evidence that the samples have not been tampered with enroute to the laboratory.

Upon receipt of the cooler at the laboratory, the cooler will be inspected by the laboratory Sample Custodian. The condition of the cooler and seal will be noted on the chain-of-custody form by the Sample Custodian.

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Analyses	*Sample Containers*	*Preservation*	*Maximum Holding Time from Sample Collection* [1]	*Volume of Sample*	*Shipping*	*Normal Packaging*
Groundwater/Residential Wells						
SVOC, PCB Pesticides	Two 1-liter amber glass bottles per analysis	Iced, 4° C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottles	Overnight or Hand Deliver	Bubble Pack or Foam Chips
VOC	Three 40-mL teflon lined septum vials	HCl to pH <2, Iced, 4° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner
Metals	One 1-liter plastic bottle	HNO3 to pH <2,	6 months (mercury - 28 days) for analysis	Fill to shoulder of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Total Cyanide	One 500-mL plastic or glass bottle	NaOH to pH>12, Iced, 4° C	14 days for analysis	Fill to shoulder of bottle	Overnight or Hand Deliver	Bubble Pack or Foam Chips
Sediment						
SVOC, Pesticides/PCB	Two 4-ounce glass jars	Iced, 4° C	14 days for extraction 40 days after extraction for analysis	Fill to neck of jars	Overnight or Hand Deliver	Bubble Pack of Foam Chips
VOC	Two 4-ounce glass jars	Iced, 4° C	14 days for analysis	Fill completely	Overnight or Hand Deliver	Bubble Pack of Foam Chips
Air						
VOC	One 6-L Summa® passivated stainless steel canister	None	30 days for analysis [2]	[3]	Overnight or Hand Deliver	Bubble Pack of Foam Chips

[1] These are technical holding times, i.e. are based on time elapsed from time of sample collection.

[2] There are no recommended canister air sampling holding time periods presently specified by EPA protocols. A thirty day holding time period for analyses specified by the Contract Laboratory Program draft Statement of Work for Air Toxics will be observed.

[3] For the air samples submitted for VOC analyses, grab samples are collected by opening the canister valve for a specified period of time or by using a calibrated critical orifice as a sampling device. The sample is taken to a point just below atmospheric pressure, so that the presence of a slight vacuum in the canister ensures that leakage has not occurred prior to analysis.

The Sample Custodian then will check the contents of the cooler with those samples listed on the chain-of-custody form. Any damage to the samples or discrepancies in sample identifications will be recorded in the remarks column of the chain-of-custody form and dated and signed. The Sample Custodian will inform the laboratory Project Manager of the problem who will contact CRA for resolution.

12.4.3 Sampling Protocols

12.4.3.1 Surface Water Sampling

Surface water samples will be collected in accordance with the following protocols:

1. New disposable gloves will be used when collecting each surface water sample. Additional new glove changes will be made as conditions warrant.

2. Samples will be collected by the grab sample method directly into precleaned sample containers. To obtain the sample, the sampler will approach the sample location from the downstream direction, invert the sample container prior to submergence (to avoid collecting debris floating on the surface) and then tilt the sample container in an upstream direction to permit the sample container to fill. To the extent possible, liquids will be collected a few inches below the surface and such that the collection container does not contact the sediment bed. When the container is full, it will be removed from the stream (in a manner that will ensure that no debris floating on the surface enters the sample container) and capped. Care will be taken to ensure that the cap interior is not handled.

3. Container preservation shipping and packaging requirements will be in accordance with Table 12.7.

12.4.3.2 Sediment Sampling

To the extent possible, sediment samples will be collected from locations underlying or immediately adjacent to the surface water sampling points. Sediment will be collected according to the following protocol:

1. Surface water samples of a particular location will be collected before sediment samples.

2. The sampling tool and all other instruments used in extracting the sediment samples will be precleaned between each sampling location using the prescribed decontamination procedure detailed in Section 12.4.1.

3. A new pair of disposable gloves will be used for each sample handled. Additional glove changes will be undertaken as conditions warrant.

4. Sediment samples will be collected with a spoon utensil manually scraping the upper two inches of the ditch bed.

5. Each sample (or portion thereof) collected will be placed directly in the appropriate sample container. Care will be taken to ensure that the cap interior is not handled.

6. Container, preservation, shipping and packing requirements will be in accordance with Table 12.7.

12.4.3.3 Groundwater Monitoring Well Sampling Protocols

Groundwater samples will be obtained using the sampling protocol which follows:

1. The depth of water in each well will be measured to the nearest 0.01 foot using an electric tape. The measuring device will be precleaned prior to use in each well using the cleaning sequence provided in Section 12.4.1.

2. Prior to sampling, each well will be purged using a precleaned, stainless steel bottom-filling bailer or a stainless-steel outer casing submersible sampling pump. The monitoring wells will be purged by removing a minimum of three standing well volumes of groundwater where the volume of standing water is calculated as follows:

$$V = 0.041\ d^2\ h$$

where:

V	=	volume of standing water in gallons
d	=	diameter of the well in inches
h	=	depth of water in feet

Field measurements of pH, conductivity and temperature of the evacuated water will be obtained and recorded following removal of each standing well volume and prior to sample collection. Well purging will continue until three consecutive and consistent readings (± 0.2 units for pH, ± five percent for conductivity and ± two degrees for temperature) of pH, conductivity and temperature are obtained or a maximum of five standing well volumes have been removed. In the event that a well is bailed dry prior to achieving three well volumes, groundwater will be permitted to recover to a level sufficient for sample collection. The time that the well was bailed dry will be

recorded and the well will be monitored for recovery. Upon recovery, the sample will be collected. All waste groundwater not collected for analysis will be disposed of in the on-Site treatment system.

3. After purging the required volume of well water or immediately after well development, water samples will be collected using a pre-cleaned stainless bailer attached to polypropylene rope. The bailer will be emptied directly into the appropriate sample containers. Containers will be filled in order of decreasing analyte volatility, using techniques which will minimize sample agitation. New polypropylene rope will be used for each monitoring well.

4. Unfiltered groundwater samples will be collected for inorganic analysis. The protocols for placing samples in appropriate containers, preservation and shipping are included in Table 12.7.

5. A field duplicate sample will be collected at a frequency of one per ten investigative samples collected or at a minimum of one per sampling event. Sample containers will be filled in order of decreasing analyte volatility.

6. Samples will be collected for MS/MSD and MS/DUP analysis at a frequency of one per twenty investigative samples. The sample for MS/MSD and MS/DUP analysis will be collected from a well representative of the condition of the majority of the monitoring wells, turbid or non turbid. Samples will be collected from the representative monitoring wells using the same protocol as for the field duplicate with increased sample volume being collected for organics analyses. The chain-of-custody forms sent to the project laboratory will indicate the samples collected for MS/MSD and MS/DUP analysis.

7. A field (rinsate) blank sample will be collected at a frequency of one per ten investigative samples collected or at a minimum of one per

sampling event. This sample will consist of deionized water poured into, and then sampled out of, a precleaned bailer. This will provide a quality assurance check on the decontamination procedures employed for the bailers and sample containers.

12.4.3.4 Residential Well Sampling

The residential wells will be sampled according to the following protocol:

1. Water will be collected, if possible, from an outdoor spigot. The sampler should avoid taking the sample after flow through a water softener or home water treatment system.

2. Water will be allowed to run through the tap for fifteen minutes in order to purge the water system. Purged water will not be collected for disposal.

3. Samples will be collected as closely to the well heads as possible, and will be collected directly into sample containers in order of decreasing analyte volatility. VOCs will be collected first followed by SVOCs, pesticides/PCBs and inorganics. Samples from residential wells will not be filtered.

4. Three residential wells will be included in the monitoring program. The residential wells to be sampled will be selected by USEPA and Ohio EPA prior to each sampling round.

5. Container, preservation, shipping and packaging requirements will be in accordance with Table 12.7.

12.4.3.5 Treatment System Water

The influent and effluent waters will be sampled according to the following protocol:

1. Water will be collected from the appropriate sample tap.

2. Water will be allowed to run through the sample tap for one minute in order to purge the water system. Purged water will be collected and dispose of using the treatment system.

3. Samples will be collected directly into sample containers in order of decreasing analyte volatility.

4. Container, preservation, shipping and packaging requirements will be in accordance with Table 12.7.

12.4.3.6 Air Sampling

Samples of air emissions from the vapor phase carbon adsorber vents will be collected using the following protocol:

1. A short sampling probe will be inserted into the vent and attached to a pneumatic flow controlled pre-cleaned evacuated Summa® canister.

2. At the start of sampling, the canister valve will be opened to allow the emissions to flow into the canister. The pneumatic flow controller will be calibrated to a flow rate of approximately 100 mL per minute for a one hour intergral sample of six liters.

3. Upon completion of sampling, the canister valve will be closed and the probe and controller removed.

4. The canister will be labeled and transported to the laboratory for analysis.

12.5 SAMPLE CUSTODY AND DOCUMENT CONTROL

It is USEPA and Region V Policy to follow the USEPA Region V sample custody, or the chain-of-custody protocols as described in "NEIC Policies and Procedures", EPA-330/9-78-001R, revised August 1991. This custody is in three parts: sample collection, laboratory analysis and final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area on Site.

A sample or evidence file is under your custody if it:

i) is in your possession;
ii) is in your view, after being in your possession;
iii) is in your possession and you place it in a secured location; or
iv) is in a designated secure area.

12.5.1 Field Chain-of-Custody Procedures

The sample packaging and shipment procedures summarized below will insure that the samples will arrive at the laboratory with the chain-of-custody intact. The protocol for specific sample numbering using case numbers and traffic report numbers, if applicable, and other sample designations are included in Section 12.4.

12.5.1.1 Field Procedures

1) The field sampler is personally responsible for the care and custody of the samples until they are transferred to another individual or properly dispatched to the laboratory. As few people as possible should handle the samples.

2) All bottles will be labeled with unique sample numbers.

3) Sample labels will be completed for each sample using waterproof ink.

12.5.1.2 Field Logbooks/Documentation

Field logbooks will provide the means of recording data collecting activities performed. As such, entries will be described in as much detail as possible so that persons going to the Site could reconstruct a particular situation without reliance on memory.

The title page of each logbook will contain the following:

i) person to whom the logbook is assigned;
ii) logbook number;
iii) project name;
iv) project start date; and
v) end date.

Entries into the logbook will contain a variety of information. At the beginning of each entry the date, start time, weather, names of all sampling team members present, level of personal protection being used, and the signature of the person making the entry will be entered. The names of visitors to the Site, field sampling or investigation team personnel and the purpose of their visit will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in ink with no erasures. If an incorrect entry is made, the information will be crossed out with a single strike mark. Whenever a sample is collected, or a measurement is made, a detailed

description of the location of the sampling point, which includes compass direction and distance taken from a reference point, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

Samples will be collected following the sampling procedures presented in Section 12.4. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth from which the sample was collected, volume and number of containers. Sample identification number will be assigned during sample collection. Field QC samples, which will receive an entirely separate sample identification number, will be submitted to the laboratory blind to avoid laboratory bias of field QC samples.

12.5.1.3 Transfer of Custody and Shipment Procedures

1. Samples will be accompanied by a properly completed chain-of-custody record. The sample numbers and locations will be listed on the chain-of-custody record. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to the laboratory, or to/from a secure storage area.

2. Samples will be properly packaged for shipment and dispatched to the laboratory for analysis, with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be secured with custody tape and for shipment to the laboratory. The cooler will be strapped shut with strapping tape in at least two locations.

3. Whenever samples are split with a source or government agency, a separate chain-of-custody record will be prepared for those samples and

marked to indicate with whom the samples are being split. The person relinquishing the samples to the facility or agency will request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses to sign this will be noted in the "Received By" space.

4. All shipments will be accompanied by the chain-of-custody record identifying the contents as specified in Section 12.4.2.3.

5. If the samples are sent by common carrier, a bill of lading will be used. Receipts of bills of lading will be retained as part of the permanent documentation. Commercial carriers will not be required to sign off on the custody records as long as the custody records are sealed inside the sample cooler and the custody tape remain intact.

12.5.2 Laboratory Chain-of-Custody Procedures

The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number and customer number will then be entered into the sample receiving log. The laboratory date of receipt will also be noted.

Laboratory custody procedures and document control for those samples analyzed by the project laboratory will be carried out as specified in the appropriate SOP included in Appendix 12.1.

12.5.3 Storage of Samples

After the sample custodian has prepared the receiving log, the chain-of-custody will be checked to ensure that all samples are stored in the appropriate locations. All samples will be stored within an

access-controlled location and will be maintained under the preservation requirements specified in Table 12.7 until completion of all analytical work or, as a minimum, for 30 days after receipt of the final report by CRA.

12.5.4 Final Evidence Files Custody Procedures

Evidentiary files for the entire project will be maintained by the CRA's Project Manager and will consist of the following:

i) project plan;
ii) project log books;
iii) field data records;
iv) sample identification documents;
v) chain-of-custody records;
vi) correspondence;
vii) references, literature;
viii) final data packages;
ix) miscellaneous - photos, maps, drawings, etc.; and
x) final report.

The evidentiary file materials will be the responsibility of the evidentiary file custodian with respect to maintenance and document removal.

The laboratory will be responsible for maintaining analytical log books and laboratory data. Raw laboratory data files will be inventoried and maintained by the laboratory for a period of five years, at which time the Project Manager will advise the laboratory regarding the need for additional storage.

12.6 CALIBRATION PROCEDURES AND FREQUENCY

This section describes procedures for maintaining the accuracy for all the instruments and measuring equipment which will be used for conducting field tests and laboratory analyses. These instruments and equipment will be calibrated prior to each use or on a scheduled, periodic basis.

12.6.1 Field Instruments/Equipment

Instruments and equipment used to gather, generate or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specification and the procedures in the SOPs in Appendix 12.1.

Equipment to be used during the field sampling will be examined to certify that it is in operating condition. This includes checking the manufacturer's operating manual for each instrument to ensure that all maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that the notation on any prior equipment problem are not overlooked, and all necessary repairs to equipment have been carried out.

12.6.1.1 Field Instrument Calibration

Calibration of the field instruments will be done prior to the collection of each water sample if well purging data indicate a change (>±10 percent) in pH and/or conductivity from the last location sampled. Calibration of field instruments will be conducted at least daily during groundwater sampling. The field equipment will be maintained, calibrated

and operated in a manner consistent with the manufacturer's guidelines and the field SOPs in Appendix 12.1.

12.6.2 Laboratory Instruments

Calibration of laboratory equipment will be based on approved written procedures. Records of calibration, repairs, or replacement will be filed and maintained by the designated laboratory personnel performing quality control activities. These records will be filed at the location where the work is performed and will be subject to QA audit. For all instruments, the laboratory will maintain a properly trained repair staff with in-house spare parts or will maintain service contracts with vendors.

The records of calibration will be kept as follows:

1) If possible, each instrument will have record of calibration permanently affixed with an assigned record number.

2) A label will be affixed to each instrument showing description, manufacturer, model numbers, date of last calibration and by whom calibrated (signature), due date of next calibration and compensation or correction figures, as appropriate.

3) A written stepwise calibration procedure will be available for each piece of test and measurement equipment.

4) Any instrument that is not calibrated to with the manufacturer's original specification will display an appropriate warning tag.

Specific calibration procedures are detailed in the associated SOPs presented in Appendix 12.1.

12.7 ANALYTICAL PROCEDURES

The samples collected for chemical analyses will be analyzed using the methods listed in Table 12.8 and detailed in the respective SOPs included in Appendix 12.1. The rationale for selection of the parameters is based on the Statement of Work referenced in Section 12.1. It should be noted that at the end of the first year of monitoring, the results shall be evaluated and reviewed and a Site-specific parameter (indicator) list (SSPL) will be developed and submitted to USEPA and OEPA for modification and/or approval. Samples collected from subsequent monitoring events will be analyzed for the approved SSPL.

TABLE 12.8

SUMMARY OF ANALYTICAL METHODS
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Matrix	*Parameter* [1]	*Method of Analysis*
Sediment	TCL VOC	SOP for SW-846 [2] 8240
	TCL SVOC	SOP for SW-846 3550, 8270
	TCL PCB/Pesticides	SOP for SW-846 3550, 8080
	TAL Metals	SOP for SW-846 3050, 6010/7000 series
	Cyanide	SOP for SW-846 9010
Groundwater	TCL VOC	SOP for SW-846 8240
	TCL SVOC	SOP for SW-846 3520, 8270
	TCL PCB/Pesticides	SOP for SW-846 3520, 8080
	TAL Metals	SOP for SW-846 3005, 3020, 6010/7000 series
	Cyanide	SOP for SW-846 9010
Surface Water	TCL VOC	SOP for SW-846 8240
	TCL SVOC	SOP for SW-846 3520, 8270
	TCL PCB/Pesticides	SOP for SW-846 3520, 8080
Residential Water	TCL VOC	SOP for SW-846 8260 (low level)
	TCL SVOC	SOP for SW-846 3520, 8270 (low level)
	TCL PCB/Pesticides	SOP for SW-846 3520, 8080 (low level)
	TAL Metals	SOP for SW-846 3005, 3020, 6010/7000 series (low level)
	Cyanide	SOP for SW-846 9010 (low level)
Effluent Water	OEPA VOC	SOP for SW-846 [3] 8240
	OEPA BNA	SOP for SW-846 8270
	OEPA Metals	SOP for SW-846 3005, 3020, 6010/7000 Series
Air	PPL VOC	SOP for EPA-MCA 624/TO-14 [4]

[1] TCL = Target Compound List
VOC = Volatile Organic Compounds
SVOC = Semi-volatile Organic Compounds
PCB = Polychlorinated Biphenyls
OEPA = Ohio Environmental Protection Agency final effluent monitoring requirements
BNA = Base/Neutral and Acid Extractable Organic Compounds
PPL = Priority Pollutant List

[2] SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods", EPA SW-846, 3rd edition, November 1986.

[3] EPA-MCA - "Methods for Organic Chemical Analysis of Industrial and Municipal Wastewater", EPA 600/4-82-057, July 1982.

[4] TO-14 - "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis", USEPA Compendium Method TO-14.

12.8 INTERNAL QUALITY CONTROL CHECKS AND FREQUENCY

This section presents the internal quality control checks which will be employed for field and laboratory measurements and the frequencies at which they will be performed.

12.8.1 Field QC

Quality control procedures for field measurements will be limited to checking the reproducibility of the measurement in the field by obtaining multiple readings and by calibrating the instruments (where appropriate).

Quality control of field sampling will involve collecting field duplicates and field blanks in accordance with the applicable procedures and frequencies described in Sections 12.3.1 and 12.4, and the level of effort indicated in Table 12.1.

12.8.2 Laboratory QC

Specific procedures related to internal laboratory QC samples (namely, matrix spikes, surrogate spikes, blanks, QC check samples and matrix spike duplicates) are detailed in the following subsections.

The internal QC checks for the methods of analyses will follow the appropriate methods specified in Table 12.8, and criteria outlined in the applicable SOPs presented in Appendix 12.1.

12.8.2.1 Initial and Continuing Calibration Checks

The compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. The initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of an analysis run, while the continuing calibration checks document that the initial calibration is still valid, and that satisfactory maintenance and adjustment of the instrument on a day-to-day basis is achieved. The specific control criteria and action requirements for these calibrations will be as specified in the SOPs presented in Appendix 12.1.

12.8.2.2 Internal Standards Performance

The internal standards performance criteria ensure that GC/MS sensitivity and response is stable during every run. Acceptance criteria will be as specified in the referenced methods and detailed in the SOPs presented in Appendix 12.1.

12.8.2.3 Method Blank Samples

A method blank sample will be analyzed by the laboratory at a frequency of one blank per twenty analyses or, in the event that an analytical round consists of less than twenty samples, one method blank sample will be analyzed. The method blank sample, an aliquot of analyte-free water or suitable solid material (sodium sulfate, Ottawa sand), will be carried through the entire analytical procedure.

12.8.2.4 MS/MSD and MS/DUP Samples

A MS/MSD sample set will be analyzed at a minimum frequency of one per twenty organic investigative samples. A MS/DUP or MS/MSD sample set will be analyzed for inorganic analyses at the same frequency as MS/MSD samples. Acceptance criteria and compounds that will be used for matrix spikes are identified in the SOPs in Appendix 12.1. Percent spike recoveries will be used to evaluate analytical accuracy while relative percent difference between the spike and matrix spike duplicate will be used to assess analytical precision.

12.8.2.5 Surrogates

Surrogates are used in all GC and GC/MS analyses. Every blank, standard, and environmental sample including MS/MSD samples will be spiked with surrogate compounds prior to purging volatiles or extracting semi-volatiles.

Surrogates will be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries will fall within the control limits set by procedures specified in the method for analytes falling within the quantitation limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates out of the quantitation limit; assessment of analytical quality in these cases will be based in the quality control embodied in the check, matrix spike and matrix spike duplicate samples. Surrogate compounds recovery control limits will be those presented in the SOPs in Appendix 12.1.

12.8.2.6 Laboratory Duplicate Analysis

Laboratory duplicate analyses are indicators of laboratory precision based on each sample matrix used for inorganic analyses associated with this project. Specified control criteria and action levels will be consistent with that specified in the SOPs in Appendix 12.1.

12.8.2.7 Blind Check Samples

As supplied by the agencies, an analytical batch may contain a blind check sample. In general, the blind check sample will be obtained from USEPA or OEPA and supplied to CRA. The analytes employed in this check sample will be a representative subset of the analytes of interest. The percent recovery will be calculated for analytes from the check samples as defined in Section 12.12.3.

12.8.2.8 Trip Blank Samples

Trip blank samples will be submitted with volatile organic monitoring well samples only, and will be used to determine if cross-contamination occurs during the shipment of investigative samples. Trip blank samples are prepared in the laboratory, prior to the sampling event, by filling two preserved 40-mL vials with organic-free deionized water. The trip blank samples are kept with the investigative samples throughout the duration of the sampling event, and upon return to the laboratory, are analyzed for VOC to determine the presence of organic compounds introduced during storage and shipment.

12.9 DATA REDUCTION, VALIDATION AND REPORTING

The project laboratory will perform analytical data reduction and review in-house under the direction of the laboratory QA Officer. The laboratory QA Officer will be responsible for assessing data quality and advising of any data which were rated "preliminary" or "unacceptable" or other qualifications based on the established QC criteria. The laboratory will provide Level III (or equivalent) deliverables. Data reduction, review and reporting by the laboratory is typically conducted as detailed in the following procedure.

1. Raw data produced and checked by the responsible analyst is turned over for independent review by another analyst.

2. The area supervisor reviews the data for attainment of quality control criteria established by the QAPP.

3. The area supervisor will decide whether any sample re-analysis is required.

4. Upon completion of all reviews and acceptance of the raw data by the supervisor, a report will be generated and sent to the Project Manager.

5. The Project Manager will complete a thorough inspection of all reports.

6. Upon acceptance of the preliminary reports by the Project Manager, final reports will be generated and signed by the laboratory Operations Manager or his designee.

7. A thorough review of a percentage of all data packages is performed by the laboratory Quality Assurance Officer or his designee.

Field data from direct-reading instruments (pH, conductance, temperature) will not require reduction. Laboratory data reduction will be performed using the equations in the SOPs provided in Appendix 12.1.

CRA's QA/QC Officer - Analytical and Field Activities will conduct an evaluation of data reduction and reporting by the laboratory. These evaluations will consider the finished data sheets, field blank data and recovery data for surrogate and matrix spikes. The material will be checked for legibility, completeness, correctness and the presence of requisite dates, initials, and signatures. The results of these checks will be assessed and reported to the Engineering Consultant's Project Manager noting any discrepancies and their effect upon the acceptability of the data. All information garnered for QA/QC checks will be discussed in a QA/QC Validation report.

Validation of the analytical data will be performed by CRA's QA/QC Officer - Analytical and Field Activities based on the applicable evaluation criteria outlined in "National Functional Guidelines for Organic Data Review", Draft December 1990, revised June 1991 and "Laboratory Data Validation Functional Guidelines for Evaluating Inorganics Analysis", Draft October 1989. The assessment of analytical and field data will include checks for adherence to laboratory QA procedures and accuracy and precision criteria; and the presence of transmittal errors and anomalously high or low parameter values. The results of these data validations will be reported to the Project Manager, noting any problems and their effect upon the acceptability of the data.

Data produced from field measurements and sample collection activities that are used in the project reports will be appropriately identified and appended to the report. Where data have been reduced or summarized, the method of reduction will be documented in the report. In

addition, field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

Laboratory data packages for chemical analyses will consist of the following deliverables:

i) a case narrative that includes a summary of analytical methods used and a description of any unusual action or conditions;

ii) dates of sample receipt, extraction/digestion and analysis;

iii) laboratory and field sample identification numbers;

iv) samples results in tabular format;

v) method blank sample summaries;

vi) surrogate compound recovery data and control limits;

vii) MS/MSD and MS/DUP recovery and RPD data and control limits;

viii) check sample data; and

ix) executed chain-of-custody forms.

The data packages will be stored with the evidentiary files as described in Section 12.5.4. The USEPA and OEPA, upon request, will receive (within 30 days of receipt) all raw data packages from the project laboratories.

12.10 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits of both field and laboratory activities will be conducted to verify that sampling and analysis are performed in accordance with the procedures established in the QAPP. The audits of field and laboratory activities include two separate independent parts: internal and external audits.

12.10.1 Field Audits

Internal audits of field activities (sampling and measurements) will be conducted by the QA/QC Officer - Analytical and Field Activities. The audits will include examination of field sampling records, field instrument operating records, sample collection, handling and packaging compliance with the established procedures, maintenance of QA procedures, chain-of-custody, etc. These audits will be conducted to correct deficiencies, and to verify that QA procedures are maintained throughout the remediation. The audits will involve review of field measurement records, instrumentation calibration records and sample documentation.

Any external audits will be conducted by OEPA or USEPA Region V.

12.10.2 Laboratory Audits

The internal performance and system audits of the laboratory may be conducted by the QA/QC Officer. The system audits, which will be conducted as deemed necessary by the CRA's Project Manager or QA/QC Officer - Analytical and Field Activities and will include examination of laboratory documentation of sample receiving, sample log-in, sample storage, chain-of-custody procedure, sample preparation and analysis,

instrument operating records, etc. The performance audits will be conducted on a quarterly basis. Blind QC samples will be prepared and submitted along with project samples to the laboratory for analysis throughout the project. The laboratory QA Officer will evaluate the analytical results of these blind performance samples to ensure the laboratory maintains acceptable performance.

Any external audits of the laboratories will be conducted by OEPA or USEPA Region V.

12.11 PREVENTIVE MAINTENANCE

All analytical instruments to be used in this project will be serviced by the laboratory personnel at regularly scheduled intervals in accordance with the manufacturer's recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of the laboratory personnel will be performed by the equipment manufacturer or its designated representative.

Daily checks of each instrument will be by the analyst who has been assigned responsibility for that instrument. This will include changing GC inlet liners, tuning GC/MS, checking operation of data systems, checking for leaks, etc. Manufacturer's recommended procedures will be followed in every case.

Table 12.9 presents routine preventive maintenance for laboratory and field instruments.

TABLE 12.9

ROUTINE PREVENTIVE MAINTENANCE PROCEDURES AND SCHEDULES SUMMIT NATIONAL SUPERFUND SITE DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Gas Chromatograph/Mass Spectrometer (GC/MS)	1. Replace pump oil as needed. 2. Change septa weekly or as often as needed. 3. Change gas line dryers as needed. 4. Replace electron multiplier as often as needed. 5. Replace gas jet splitter as needed. 6. Replace GC injector glass liner weekly or as often as needed. 7. Replace GC column as needed. 8. Check to ensure that gas supply is sufficient for the day's activity, and the delivery pressures are set as described in the SOP. 9. Check to ensure the pressure on the primary regulator never runs below 100 psi.	1. Syringes 2. Septa 3. Various electronic components 4. Glass jet splitter 5. GC column 6. Glass liner
Gas Chromatograph	1. Change septa weekly or as often as needed. 2. Change gas line dryers as needed. 3. Replace GC injector glass liner weekly or as often as needed. 4. Replace GC column as needed. 5. Clean/replace GC detector as needed. 6. Check to ensure that gas supply is sufficient for the day's activity, and the delivery pressures are set as described in the SOP. 7. Check to ensure the pressure on the primary regulator never run below 100 psi.	1. Syringes 2. Septa 3. Detectors 4. Glass liner 5. GC column

TABLE 12.9

**ROUTINE PREVENTIVE MAINTENANCE
PROCEDURES AND SCHEDULES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO**

Purge and Trap Sample Concentrator	1. Replace trap as needed. 2. Decontaminate the system after running high concentration samples or as required by blank analysis. 3. Leak check system daily and as often as needed 4. Check to ensure the gas supply is sufficient for the day's activity, and the delivery pressures are set as described in the SOP. 5. Check to ensure the pressure on the primary regulator never run below 100 psi.	1. Spare traps 2. Spare sparger 3. Various electronic components/ circuits 4. Plumbing supplies - tubing fitting
Graphite Furnace Atomic Spectrophotomer (GFAA)	1. Change graphite tube contact rings as needed. 2. Change D2 background correction lamp. 3. Clean quartz window as necessary. 4. Check to ensure the gas supply is sufficient for the day's activity, and the delivery pressures are set as described in the SOP. 5. Check graphite tubes and replace as necessary.	1. Contact rings 2. D2 arc lamp 3. Spare lamps
Mercury Analyzer	1. Clean tubing and quartz cell weekly or as often as needed. 2. Clean aspirator as necessary. 3. Check to ensure the gas supply is sufficient pressures are set as described in the SOP.	1. Quartz cells 2. Aspirator

TABLE 12.9

**ROUTINE PREVENTIVE MAINTENANCE
PROCEDURES AND SCHEDULES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO**

Inductively Coupled Plasma Spectrometer (ICP)	1. Clean torch assembly and mixing chamber when discolored or after eight hours of running high dissolved solid samples 2. Clean nebulizer as needed. 3. Check to ensure the gas supply is sufficient for the day's activity pressures are set as described in the SOP.	1. Spare torch mixing chambers 2. Spare nebulizer
pH Meter	1. Check battery (if used in field); and replace if discharged. 2. After use in samples containing free oil, wash the electrode in soap and rinse thoroughly in water. Immerse the lower third of the electrode in diluted HCl (1:9) solution for 10 minutes to remove any film formed. Rinse thoroughly with water. 3. Keep electrode properly filled with appropriate filling electrolyte solution.	1. Standard buffers 2. Electrolyte filling solution 3. Spare electrode
Specific Conductivity Meter	1. Check battery (if used in field); and replace 2. After use in samples containing free oil, wash the electrode in soap and rinse thoroughly with water.	1. Standard solution if discharged 2. Spare electrodes

TABLE 12.9

ROUTINE PREVENTIVE MAINTENANCE
PROCEDURES AND SCHEDULES
SUMMIT NATIONAL SUPERFUND SITE
DEERFIELD TOWNSHIP OF PORTAGE COUNTY, OHIO

Electric Water Level Meter	1. Check battery and replace if needed. 2. Check connection between probe and tape periodically. Repair with electrical tape if required. 3. After use, wash the probe and reel in soap and rinse thoroughly with distilled water	1. Probes, tapes, cable reels, batteries

12.12 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy and completeness achieved during the associated sample analyses.

12.12.1 Field Measurements

Field data will be assessed by the QA/QC Officer Analytical and Field Activities who will review the field results for compliance with the established QC criteria that are specified in the QAPP. Accuracy of the field measurements will be assessed using daily instrument calibration, calibration check, and analysis of blanks. Precision will be assessed on the basis of the reproducibility of duplicate readings of a single sample. Data completeness will be calculated using the following equation:

$$\text{Completeness (\%)} = \frac{\text{Valid (Usable) Data Obtained}}{\text{Total Data Planned}} \times 100$$

The required level of completeness will be 90 percent or greater.

12.12.2 Laboratory Data

Laboratory results will be assessed for compliance with required precision, accuracy, completeness and sensitivity as follows:

12.12.2.1 Precision

Precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD for organic analysis, and MS/MSD or laboratory duplicate analyses for inorganic analysis. The relative percent difference (RPD) will be calculated for each pair of duplicate analyses as discussed in Section 12.12.3.

12.12.2.2 Accuracy

Accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections 12.3 and 12.8 of the QAPP using the analytical results of method blanks, reagent/preparation blank, MS/MSD samples, field blank and trip blanks. The percent recovery (%R) of matrix spike samples will be calculated as discussed in Section 12.12.3.

12.12.2.3 Completeness

Completeness will be assessed by comparing the number of usable results to the total possible number of results using the formula presented in Section 12.12.1. The required level of completeness for laboratory analyses will be 90 percent or greater.

12.12.2.4 Sensitivity

The achievement of targeted quantitation limits depend on instrumental sensitivity and matrix effects. Therefore, it is important to monitor the instrumental sensitivity to ensure the data quality through constant instrument performance. The instrumental sensitivity will be monitored through the analysis of method blank and calibration check standards.

12.12.3 Statistical Evaluations

In examination of data and determination of its precision and accuracy, standard statistical formulae will be used.

12.12.3.1 Arithmetic Mean

The arithmetic mean is the average obtained by dividing a sum by the number of its addends. A number of recovery results are averaged together to improve the accuracy of the measurement. Figure 12.3, equation 1 summarizes the formula to be used to determine the arithmetic mean.

12.12.3.2 Standard Deviation

The standard deviation is the square root of the average squared difference between the individual values and the average value. A number of recovery results are evaluated to find the numerical variation in the data which is then used in the determination of the percent relative standard deviation. Figure 12.3 equation 2 summarizes the formula to be used to determine the standard deviation.

12.12.3.3 Percent Relative Standard Deviation (%RSD)

The percent relative standard deviation is obtained by dividing the standard deviation of the values by the arithmetic mean of the values. The %RSD is calculated on a series of measurements to evaluate an

Equation 1 Determination of Arithmetic Mean ($\bar{X}$)

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where n = number of measurements

X_i = value of measurements

Equation 2 Determination of Standard Deviation (σ_{n-1})

$$\sigma_{n-1} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n-1}}$$

where n = number of measurements

X_i = value of measurements

$\bar{X}$ = arithmetic mean

Equation 3 Determination of Percent Relative Standard Deviation (% RSD)

$$\% \text{ RSD} = \frac{\sigma_{n-1}}{\bar{X}} \times 100$$

where σ_{n-1} = standard deviation

$\bar{X}$ = arithmetic mean

Equation 4 Determination of Percent Recovery (% R)

$$\% \text{ R} = \frac{SSR - SR}{SA} \times 100$$

where SSR = Spiked Sample Result

SR = Sample Result or Background

SA = Spike Added

Equation 5 Determination of Relative Percent Difference (RPD)

$$RPD = \left(\frac{|R_1 - R_2|}{\left[\frac{R_1 + R_2}{2}\right]} \right) \times 100$$

where R_1 = value of first result

R_2 = value of second result

figure 12.3

STATISTICAL FORMULAE
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CRA

instruments analytical precision (e.g., initial calibration). Figure 12.3, equation 3 summarizes the formula to be used to determine %RSD.

12.12.3.4 Percent Recovery (%R)

The percent recovery of a parameter is obtained by dividing the amount recovered by the true amount added and multiplying by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. Figure 12.3, equation 4 summarizes the formula to be used to determine the percent recovery.

12.12.3.5 Relative Percent Difference (RPD)

The relative percent difference is obtained by dividing the difference between two numbers by their arithmetic mean and multiplying by 100. The RPD is used to evaluate the analytical precision of two replicate measurements (e.g., matrix spike/matrix spike duplicate). Figure 12.3, equation 5 summarizes the formula to be used to determine RPD.

12.13 CORRECTIVE ACTION

Corrective action is the process of identifying, recommending, approving and implementing measures to counter unacceptable procedures or out of quality control performance which can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation and data assessment. All corrective action proposed and implemented will be documented.

12.13.1 Field Corrective Action

Corrective action in the field may be necessary when the sample network is changed (i.e. more/less samples, sampling locations other than those specified in the QAPP), sampling procedures and/or field analytical procedures require modification, due to unexpected conditions. USEPA and OEPA will be notified of any field changes. In general, the field sampling team may identify the need for corrective action. The field sampling team, in consultation with the QA/QC Officer - Analytical and Field Activities, will recommend a corrective action. The QA/QC Officer - Analytical and Field Activities will approve the corrective action which will be implemented by the field team. It will be the responsibility of the QA/QC Officer - Analytical and Field Activities to ensure the corrective action has been implemented.

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The QA/QC Officer - Analytical and Field Activities will identify deficiencies and recommended corrective action to the Project Manager. Implementation of corrective actions will be performed by the QA/QC Officer - Analytical and Field Activities and field team. Corrective action will be documented in quality assurance reports to management.

12.13.2 Laboratory Corrective Action

Corrective action in the laboratory may occur prior to, during and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, potentially high concentration samples may be identified during sample log-in or just prior to analysis. Following consultation with analysts and section leaders, it may be necessary for the laboratory QA Officer to approve the implementation of corrective action. The submitted SOPs specify some conditions during or after analysis that may automatically trigger corrective action or optional procedures. These conditions may include dilution of samples, additional sample extract cleanup or automatic reinjection/reanalysis when certain QC criteria are not met.

The calibration acceptance/rejection criteria presented in the SOPs presents examples of situations requiring corrective action for each analytical instrument. In addition, the SOPs in Appendix 12.1 each provide a section on corrective action requirements.

The bench chemist will identify the need for corrective action. The Operations Manager or section leaders, in consultation with the laboratory supervisor and staff, will approve the required corrective action to be implemented by the laboratory staff. The laboratory QA Officer will ensure implementation and documentation of the corrective action.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action report and the case narrative report sent from the laboratory.

The need for corrective action may also be identified during systems or performance audits. In these cases, the need for corrective action will be identified by the auditor and the corrective action taken to resolve the problem will be documented by the laboratory QA Manager. The corrective action taken will depend upon the QA/QC criteria which was violated. All problems requiring corrective action and the corrective action taken will be reported to the laboratory Project Manager.

12.13.3 Corrective Action During Data Validation and Data Assessment

The QA/QC Officer - Analytical and Field Activities may identify the need for corrective action during either the data validation or data assessment. Potential types of corrective action may include resampling by the field team or re-injection/reanalysis of samples by the laboratory.

These actions are dependent upon the ability to mobilize the field team, whether the data to be collected is necessary to meet the required quality assurance objectives (e.g. the holding time for samples is not exceeded). When the QA/QC Officer - Analytical and Field Activities identifies a corrective action situation, the Project Manager will be responsible for approving the implementation of corrective action, including resampling, during data assessment.

12.14 QUALITY ASSURANCE REPORT TO MANAGEMENT

Management (including USEPA and OEPA) will receive reports on the performance of the measurement system and data quality on an annual basis. These reports will be included in the evaluation reports on the effectiveness monitoring program that will be submitted to USEPA and OEPA on an annual basis.

Minimally, these reports will include:

1. assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;
2. any changes in the QA/QC program;
3. results of system audits; and
4. QA problems, action taken and resolutions.

The QA/QC Officer - Analytical and Field Activities will be responsible within the organizational structure for preparing these reports. The final report for the project will also include a separate QA section which will summarize data quality information contained in the periodic QA/QC reports to management, and details an overall data assessment and validation in accordance with the data quality objectives outlined in this QAPP.

APPENDIX 12.1

FIELD AND LABORATORY STANDARD OPERATING PROCEDURES

TABLE OF CONTENTS

pH/TEMPERATURE

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Potentiometric

Reference: "Methods for Chemical Analysis of Water and Wastes:", EPA-600/4-79-020, revised March 1983, Method 150.1

Sensitivity: 0.01 pH unit; 0.1 °C

Optimum Range: pH 1.00 to 12.00; temperature 0 to 100 °C

Sample Handling: Determined on site

Reagents and Apparatus:

1. Temperature compensated pH meter, Fisher Scientific Accumet Series 1000 or equivalent;
2. Combination pH electrode;
3. Temperature sensor;
4. pH buffer solutions, pH 4.00, 7.00, and 10.00 (certified buffer solutions);
5. Deionized water in wash bottle.

Calibration:

1. Press On/Off key to turn meter on. If pH indicator in main display area is not on, press pH key to place meter in pH mode.

   Main display will show pH reading. If ATC probe is attached, temperature reading will appear in center display. If meter was previously standardized, buffers used will be shown in lower display.

2. Set pH display resolution by pressing Exp key until desired resolution is shown.

3. Clear current standardization points by pressing Stdz key. Then, within four seconds, press Clear key. Current standardization points will be removed from instrument memory.

4. Immerse electrodes in pH 4.00 buffer. Press Stdz key to begin standardization.

   Nominal (25 °C) value for buffer will begin flashing in lower, Standardization Values display. Main display will track electrode output in millivolts. When electrode output stabilizes, buffer value will cease flashing and remain on.

5. Rinse electrodes and immerse in pH 7.00 buffer. Press Stdz key to begin standardization with this buffer.

   In lower display, nominal (25 °C) value for second buffer will begin flashing, while value for first buffer remains on. Main display will track electrode output in millivolts. When electrode output stabilizes, second buffer value will cease flashing and also remain on.

6. Rinse electrodes and immerse in pH 10.00 buffer. Press Stdz key to begin standardization with this buffer.

   In lower display, nominal (25 °C) value for third buffer will begin flashing, while values for first and second buffers remain on. Main display will track electrode output in millivolts. When electrode output stabilizes, third buffer value will cease flashing and also remain on.

7. Rinse electrode with deionized water and place in pH 7.00 buffer. If meter reading is not 7.00, follow Steps 4 to 7 again.

Procedure:

1. Calibrate meter using calibration procedure.

2. Pour the sample into clean sample jar or plastic cup.

3. If stability bar is not currently on, press Auto key. Otherwise, press pH key. This initiates measurement of first sample pH.

   Stability bar will flash and main display will begin to track sample pH. When both electrode output and ATC stabilize, stability bar will remain on with pH reading locked.

4. Record temperature and pH of the sample in the logbook.

5. Repeat steps 3 and 4 for each sample.

6. Recheck calibration with pH 7.00 buffer solution after a minimum of every 10 samples and after the last sample.

Quality Control:

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be ±0.2 pH units.

   If the results are outside of the control limits, rinse electrodes and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below). If drift is suspected to be the cause of the problem, clean the electrode and recalibrate. If drift is still apparent, replace electrode.

2. Calibration check results must be ±0.10 pH unit of the true value. If the result is outside of ±0.10 pH unit, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in control calibration.

3. All glassware is to be soap and water washed, tap rinsed and deionized water rinsed prior to analyses unless pre-cleaned sample jars are used.

Interferences:

Interferences in pH measurements occur with presence of weak organic and inorganic salts and oil and grease. If oil and grease are visible, note in logbook. Clean electrode with soap and water, followed by 10% HCl and deionized water. Then recalibrate meter before analysis of next sample.

CONDUCTIVITY

Scope and Application: This method is applicable to surface water, wastewater and groundwater.

Method: Specific Conductance

Reference: "Methods for Chemical Analysis of Water and Wastes" EPA-600/4-79-020, revised March 1983, Method 120.1

Sensitivity: 10 µmhos/cm

Optimum Range: 10-20,000 µmhos/cm

Sample Handling: Determine on site

Reagents and Apparatus:

1. Conductivity meter - Cambridge Scientific Industries Model 301353 or equivalent;
2. Deionized water;
3. Conductivity standard, 1,413 µmhos/cm @ 77 °F (0.01 M KCl).

Notes:

The conductivity meter is factory calibrated. The calibration is checked using a solution of known conductance and recalibrated, if necessary.

Recalibration:

To recalibrate conductance, remove black plug revealing the adjustment potentiometer screw. Add standard solution to cup, discard and refill. Repeat procedure until the digital display indicates the same value twice in a row. Adjust the potentiometer until the digital display indicates the known value of conductance. To increase the digital display reading, turn the adjustment potentiometer screw counterclockwise (clockwise to decrease).

Procedure:

1. Rinse the inside of sample cup with liquid to be measured. (This is especially important if samples with a wide range of conductivity are to be measured.)

2. Fill sample cup.

3. Fill sample cup at least 2/3 full. If the sample is hot boiler water, allow to cool to 160 °F or below.

4. Slide the right hand function switch to "TEMP" and push the "READ" button. If temperature reading is not stable, empty and refill cup several times to bring cup and sample to the same temperature.

5. Read the temperature on the digital display panel and adjust both temperature compensation knobs accordingly.

6. If the approximate conductance is known, slide the left hand range selector switch to the proper range.

   Example: If you expect the sample to be around 2,000 µmhos, slide the left hand selector switch to x 1,000.

7. Slide the right hand function switch to "COND" and push the "READ" button.

8. Multiply the digital display reading by the factor indicated by the position of the left hand range switch to determine conductance.

   Example: A display reading of 1.00 with the left hand range selector switch indicating x 1,000 is:

   1.00 x 1,000 or 1,000 µmhos/cm

   Note: If a single "1" appears on the left hand side of the digital display, the sample conductance is higher than the selected range. Slide the left hand (range) selector switch in one step intervals until a 3 or 4 digit display appears.

   Conversely, if a decimal display appears (such as 0.11) move the range selector switch to the left until a 3 or 4 digit number, 1.00 or larger, appears on the display. This puts the unit in a range affording the best accuracy. Caution: A single "1" always means that the conductance is higher than the selected range.

9. Repeat steps 1 through 8 for remaining samples.

Quality Control:

1. The quality control calibration check standard must be analyzed initially, after a minimum of every 10 samples and after the last sample. If less

than 10 samples are analyzed, the calibration standards are still required. The standards must be within ±10 percent of the true value or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the field logbook.

2. Duplicate a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicate values are to be within ±15% of each other. If outside of this range, reanalyze the samples. If still outside the acceptance range, recollect sample and reanalyze. If still out, replace meter.

APPENDIX A

DEFINITIONS

Acceptable Quality Level (AQL) - "...(T)he maximum % defective or the maximum number of defective per 100 units that for the purposes of sampling inspection can be considered satisfactory as a process average." (MIL-STD-105D). A 1% AQL indicates that if a large number of lots are inspected using the sampling plan for a 1% AQL, LSG runs the risk of delivering 1% defective lots. It does indicate that 1% of the data will be defective.

Acceptance Limits - Quantitative limits placed on the precision or accuracy of quality control checks. When acceptance limits are exceeded, corrective action and/or qualification of associated sample results are required.

Accuracy - The agreement of a measurement (or the mean of multiple measurements) and the true or accepted value. Accuracy describes the bias of a measurement system. It is calculated as percent recovery, percent error, or percent difference.

Active Equipment - Equipment that is able to produce data meeting LSG's quality control requirements and whose preventive maintenance program, and documentation of same, are current.

Batch - A set of up to 20 samples and the associated quality control samples prepared for analysis together.

Blank - Material that does not contain the analytes of interest (at detectable levels) that is treated in the same manner as samples in order to monitor sampling and analysis process for the presence of contamination. There are many types of blanks which are inserted into the sampling and analysis sequence at different times:

- o Trip Blanks - Reagent water that is shipped to and from the field to monitor VOA contamination during transport and storage at the lab.
- o Field Blanks - Reagent water that is exposed to the atmosphere during sampling to monitor atmospheric contamination during sampling.
- o Equipment Blanks - Reagent water that is poured over or through a sample collection device to monitor the cleanliness of the sampling device.

- o Method or Preparation Blanks - Reagent water or, for soil/sediment/waste matrices, a blank container taken through the entire analytical process to monitor contamination introduced during laboratory processing.

- o Calibration Blanks - The solvent appropriate to the method that is introduced to the analytical system at the point of instrumental measurement to establish and/or monitor the measurement baseline.

- o Holding Blanks - Reagent water that is stored with a set of samples to monitor VOA contamination during sample storage.

Calibration - The process of establishing the relationship between measurement response and analyte mass or concentration through the measurement of materials of known analyte mass or concentration.

- o Initial Calibration - Establishment of the ratio of analytical system response to the amount of analyte present.

- o Calibration Verification - A standard prepared from a source independent of the calibration standards that is introduced to the analytical system at the point of instrumental measurement to verify the initial calibration.

- o Continuing Calibration Check - Periodic reanalysis of one of the initial calibration standards to verify the initial calibration response factor(s).

Case - A finite, usually predetermined number of samples collected over a specified period of time from a particular site for a particular project.

Comparability - The confidence with which one set of data can be compared to another.

Completeness - A measure of the amount of valid data obtained from a measurement system (i.e., data that meets quality objectives) relative to the amount that was expected to be obtained under correct normal conditions.

Contract Laboratory Program Statements of Work (CLP SOWs) - The analytical protocols defined in the current version of the "USEPA CLP Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration" and the "USEPA CLP Statement of Work for Inorganics Analysis, Multi-Media, Multi-Concentration."

Control Charting - A method for detecting lack of statistical control by evaluating the order or grouping of the observations in a set. (ASTM Manual on Quality Control of Materials, ASTM, 1951.)

Controlled Copy - A copy whose distribution is controlled in the following manner: each copy is assigned a unique identification number, recipients must acknowledge receipt of the document in writing, and revisions are provided automatically to all controlled copy holders.

Corrective Maintenance - Maintenance performed to remedy equipment malfunction.

Daily - Each day that samples are analyzed.

Data Package - Analytical results, supporting data, and narrative for one sample delivery group.

Duplicates - Two replicate measurements.

EPA Approved Methodology - Reference methods from a variety of sources that have been approved by the EPA for use in analyses performed for compliance with EPA regulations. The list of EPA-approved methods frequently includes methods from sources other than the EPA itself, including ASTM and "Standard Methods for the Examination of Water and Wastewater," APHA, AWWA, WPCF.

Inactive Equipment - Instruments and equipment that are not able to produce data meeting LSG's quality control requirements or whose preventive maintenance program, or documentation of same, are not current.

Internal Standard - A material that will be detected by the instrument, is not a target analyte, and is not found in the samples of interest. A constant amount of the internal standard is spiked into each standard, blank, sample, and quality control sample. Quantitation of target analytes is automatically adjusted for variations in internal standard response.

Lab Control Sample (LCS) - Material of known analyte concentration - a reference material or spiked blank material - that is introduced to the analytical system at the start of analysis. The LCS monitors the accuracy of sample preparation as well as instrumental measurement.

Matrix Spike (MS) - An aliquot of a sample that is spiked with a known amount of analyte at the start of analysis. Matrix spikes monitor the effects of the sample matrix, as well as laboratory processing, on the accuracy of sample results.

A Matrix Spike/Matrix Spike Duplicate (MS/MSD) is two equal aliquots of a sample that are spiked with equal amounts of analyte. MS/MSDs provide a measure of precision and accuracy.

Mean (Arithmetic) - The sum of a series of measurements divided by the number of measurements.

Percent Difference (% D) - A measure of accuracy calculated as follows:

$$\% D = \frac{M_I - M_C}{M_I} \times 100\%$$

where M_I = an Initial Measurement (e.g. RF)
M_C = the Current Measurement

Percent Error - A measure of accuracy calculated as the difference between the true or accepted value and the measured value, relative to the true or accepted value, expressed in percent. (This quantity may also be called percent difference when an initial value replaces the true or accepted value.)

Percent Recovery (% R) - A measure of accuracy calculated as follows:

- For standards and reference materials:

$$\% R_s = \frac{\text{Result}}{\text{True Value}} \times 100\%$$

- For matrix spikes (MS):

$$\% R_{ms} = \frac{SSR - USR}{SA} \times 100\%^*$$

where SSR = Spiked Sample Result
USR = Unspiked Sample Result
SA = Spike Added

*NOTE: This equation does not give a valid measure of accuracy when USR $\geq$ 4 x SA.

Performance Evaluation (PE) Sample - A reference material that is submitted for analysis as a "sample" in order to evaluate laboratory performance.

- o Blind Performance Evaluation Sample - A PE sample identified as such to the analyst, but whose true value is unknown to the analyst.

- o Double-Blind Performance Evaluation Sample - A PE sample that appears to be a routine sample to the analyst.

Precision - The agreement of a set of replicate results among themselves. Precision is measured as Range, Relative Percent Difference (RPD), or Relative Standard Deviation (RSD).

Preventive Maintenance - A program of positive actions for the reliability required to produce quality results. The program includes specification checks, calibration, cleaning, lubrication, reconditioning, adjustments, and testing.

Project - All the work done under a single contract. A project may involve several cases and extend over several months or years.

Project File - All documents relevant to a project, including sample receipt and check-in records, lab tracking records, lab notebook pages, and the data package(s).

Quality Assurance Records - The minimum amount of documentation necessary to support the validity of the work, which would allow it to be recreated if necessary, and which furnishes documentary evidence of quality.

Random Sample - A sample selection made so that all elements of the population have an equal chance of being selected.

Range - A measure of the precision of a set of replicate measurements calculated as follows:

$$\text{Range} = R_H - R_L$$

Where: R_H = the Highest Result
R_L = the Lowest Result

Reagent Water - Water that is free of the analytes of interest by virtue of distillation, deionization, and/or activated carbon treatment. In general, reagent water should meet ASTM Type II specifications.

Reference Material - Substance for which one or more established properties are used to calibrate or verify a measurement.

- o Certified Reference Material - A reference material accompanied by a certificate issued by an organization generally accepted as being technically capable to do so.

- o Standard Reference Material - Reference material certified by the National Institute of Standards and Technology (formerly the National Bureau of Standards).

Reference Method - A method as published by a recognized organization, such as the EPA, NIOSH, ASTM, etc.

Relative Percent Difference (RPD) - A measure of the precision of a two replicate measurement calculated as follows:

$$RPD = \frac{R_1 - R_2}{1/2\ (R_1 + R_2)} \times 100\%$$

where: R_1 and R_2 are the two results.

Relative Standard Deviation (RSD) - A measure of the precision of a set of replicate measurements calculated as follows:

$$RSD = \frac{s}{X} \times 100\%$$

where s = the standard deviation of the data
X = the arithmetic mean of the data

RSD is also used as a measure of the linearity of initial calibration when the RSD of the response factors of the standards is calculated.

Repeat Measurements - Two or more independent measurements of a parameter for the same sample at the same laboratory at different times.

Replicates - Samples prepared by dividing a sample into multiple aliquots that are subsequently analyzed at the same time, under the same conditions. Duplicates are considered to be two replicates.

Representativeness - A measure of the degree to which data accurately and precisely represent sampling point parameters or an environmental condition.

Response Factor (RF) - The ratio of analytical system response to analyte concentration or amount:

$$RF = \frac{\text{Response}}{\text{Standard Mass or Concentration}}$$

A Relative Response Factor (RRF) is the response factor relative to the response factor of the internal standard:

$$RRF = \frac{R_S}{C_S} \times \frac{C_{IS}}{R_{IS}}$$

where: R_S and C_S are response and concentration of the standard

R_{IS} and C_{IS} are response and concentration of the internal standard

Sample Delivery Group (SDG) - Each set of 20 field samples within a case, or each set of field samples within a case received during a 14-day calendar period (said period beginning with the receipt of the first sample in the group), whichever is more frequent.

Standardization - The use of materials of known analyte concentration to establish response factors.

Standard Deviation - The square root of the variance of a set of measurements.

Surrogate Standard - Organic compounds that are similar in chemical composition to the analytes of interest, but are not generally found in environmental samples. Surrogate standards are spiked into all blanks, standards, and samples at the start of analysis. Surrogates monitor the accuracy of sample preparation as well as instrumental measurement.

Switching Procedures - Movement to reduced or tightened inspections based on previous performance.

Test - A distinct analytical procedure that produces results for one or more analytes. (For example, the cyanide test produces only cyanide results, while the GC/MS priority pollutant volatiles test can produce results for more than 20 compounds.)

Uncontrolled Copy - A copy issued for information only. Receipt acknowledgment is not required. Subsequent revisions are not provided.

Variance (defined mathematically) - The sum of the square of the difference between each measurement within a set and the mean of the set, divided by one less than the number of values in the set.

Weekly - Each week that equipment is used for sample analysis.

LABORATORY SAMPLE TRACKING

1.0 PURPOSE AND APPLICABILITY

This section of the General Quality Assurance Plan outlines procedures for receipt, log-in, storage, and tracking samples received for analysis at fixed-base laboratories.

2.0 RESPONSIBILITIES

2.1 LOGISTIC SUPPORT GROUP LEADER

The Logistic Support Group Leader shall supervise sample receipt and log-in personnel. The Logistic Support Group Leader also arranges for sample receipt during off-hours.

2.2 SAMPLE LOG-IN CLERK

The Sample Log-in Clerk shall receive samples during normal working hours and log in all samples in a timely manner. The Sample Log-in Clerk is also responsible for notifying Laboratory Group Leaders of the receipt of samples having limited holding times.

Identify radioactive samples at check-in using the criteria provided in section 3.5.1.

2.3 PROJECT MANAGER

The Project Manager is responsible for reviewing sample log-in for completeness and accuracy with respect to parameters assigned, invoicing, and special instructions. If any anomalies are noted during log-in, the Project Manager contacts the client to resolve them. The Project Manager is also responsible for final review of deliverables.

NOTE: The Bioassay Laboratory Group Leader assumes these duties for bioassay jobs.

2.4 SAMPLE CUSTODIAN

The Sample Custodian is responsible for pH and radioactivity screening, storage and retrieval of samples, maintenance of the sample storage areas, moving samples from primary to secondary storage and, under the supervision of the Hazardous Waste Coordinator, for disposal of samples in accordance with LSG's waste handling procedures after the appropriate holding time has lapsed.

2.5 LABORATORY OPERATIONS COORDINATOR

The Laboratory Operations Coordinator is responsible for coordination of interfacility sample shipment and shipment of samples to subcontract laboratories.

2.6 RADIATION SAFETY OFFICER - DESIGNEE

The Radiation Safety Officer-Designee (RSOD) is responsible for providing log-in personnel with a list of clients and projects for which radioactive samples might be submitted for analysis, and to update the list as necessary.

The RSOD also trains sample custodians in the proper use of the uR meter for screening of incoming samples for radioactivity.

2.7 RADIOCHEMISTRY PERSONNEL

Radiochemistry lab personnel take custody of and store samples identified as radioactive materials if the RSOD is unavailable.

3.0 PROCEDURE

3.1 SAMPLE RECEIPT AND LOG-IN DURING NORMAL WORKING HOURS

3.1.1 All samples are received into the laboratory through sample receiving. When samples are received during normal working hours, the Sample Log-in Clerk, Sample Custodian, or a member of the logistic support department signs and dates the shipping manifest or airbill to acknowledge receipt of the shipping containers. Note: Airbills must be signed, dated, and retained.

3.1.2 The Sample Log-in Clerk opens the shipping containers to remove the enclosed sample documents.

CAUTION: Samples may contain potentially hazardous materials at high levels. OPEN COOLERS WITH CAUTION. If fumes are apparent or sample containers are broken or leaking, close the cooler immediately and reopen it under an operating fume hood.

EXERCISE EXTREME CAUTION WITH BROKEN OR LEAKING SAMPLES - THEY MAY CONTAIN HAZARDOUS MATERIALS. If sample tags or accompanying documentation are wet (i.e., possibly contaminated by leaking samples), seal them in a plastic bag.

3.1.3 The Sample Log-in Clerk removes the samples from the shipping container(s) and completes the laboratory sample log-in sheet (Figure 7-1 or equivalent). Analyses requested and sample bottles received are documented using test codes and bottle codes, respectively. (NOTE: In order to maintain consistency in the codes, new codes must be requested from the Quality Assurance Coordinator.)

Any anomalies with the sample containers, such as the following, are noted on a nonconformance/corrective action (NC/CA) record. (See Figure 15-1.) The NC/CA number is referenced on the log-in sheet.

- Broken or leaking sample container.

- Improper sample container.
- Improperly preserved sample (with respect to chemical or temperature preservation).
- Air bubbles in a VOA vial or TOX bottle.

3.1.4 The Sample Log-in Clerk cross-checks the information on the chain-of-custody record, air bill, sample labels, and sample tags to determine if discrepancies exist. If so, they are noted on the an NC/CA record, and the NC/CA number is referenced on the log-in sheet under anomalies. When all of the information has been recorded and cross-checked, the Sample Log-in Clerk signs and dates the laboratory sample log-in sheet.

If log-in of any samples will be delayed until questions regarding the samples, analyses requested, etc., are resolved with the client, the samples are listed on an off-hours sample receipt log (Figure 7-2 or equivalent) and placed in the sample cooler so that they are not inadvertently misplaced or forgotten. Samples on hold for more than two weeks will be returned to the client unless special arrangements are made with the Laboratory Manager.

3.1.5 The Sample Log-in Clerk physically applies a laboratory sample number to each bottle. If sample tags are received with the samples, the laboratory sample number is also applied to these. Care must be taken to ensure that the sample number does not interfere with information recorded on the sample label or tag.

The laboratory sample number consists of seven characters, as follows:

- H999999 for samples received at the Houston laboratory
- P999999 for samples received at the Pittsburgh laboratory

where "999999" is a six-digit number, which increases consecutively with each new sample number.

3.1.6 The Sample Log-in Clerk signs and dates the chain-of-custody record.

3.1.7 The Sample Log-in Clerk completes the short holding time parameters worksheet (Figure 7-3 or equivalent) for parameters with holding times $\leq$48 hours. The Inorganics Laboratory Group Leader checks this form periodically throughout the day and assigns analysis of the samples manually for the short holding time parameters.

3.1.8 If direct laboratory tracking of sample custody is to be maintained, the Sample Log-in Clerk completes the top portion of a lab tracking record (Figure 7-4).

3.1.9 Using the information on the laboratory sample log-in sheet, the Sample Log-in Clerk completes sample log-in through the LIMS. This process is explained in LSG Procedure AP-003, Program Guide for LSG's Laboratory Information Management System (LIMS).

3.2 RECEIPT OF SAMPLES FOR ANALYSIS BY CLP PROTOCOLS

Log-in and storage of samples to be analyzed by CLP protocols proceeds as described in section 3.1 above, except that an immediate work sheet (Figure 7-5 or equivalent) is prepared by the Sample Log-in Clerk. The immediate work sheet is distributed to the appropriate Group Leaders to inform them of the receipt of the samples. Following check-in review, the sample receipt and log-in documents are filed in the case file.

3.3 RECEIPT OF FIRST PRIORITY (RUSH) SAMPLES

3.3.1 Project Managers must clear acceptance of samples for first priority analysis through the Laboratory Manager or the Operations Coordinator, and inform the Logistics Support Manager of their anticipated arrival. The Project Manager then provides the Sample Log-in Clerk with the information necessary for sample log-in: client, job, analyses required, pricing, deliverables, and turnaround commitment.

3.3.2 Upon receipt of the samples, the Sample Log-in Clerk initiates log-in immediately in accordance with section 3.1 above. The Sample Custodian also performs the pH verification (see section 3.9 below) immediately. Once the laboratory tracking numbers have been applied to the sample bottles, the Sample Log-in Clerk distributes an immediate worksheet (Figure 7-5 or equivalent) to the appropriate Group Leaders, and the Sample Custodian stores the samples.

3.4 RECEIPT OF BIOASSAY SAMPLES

3.4.1 The Sample Log-in Clerk, Sample Custodian, or a member of the logistic support department sign and date the shipping manifest or air bill to acknowledge receipt of the shipping containers. The shipping containers are then forwarded to the bioassay.

3.4.2 Laboratory personnel inspect the shipping containers and samples, review the shipping documents, and complete the sample log-in sheet following LSG Procedure QA-7, sections 3.1.2 through 3.1.4, 3.1.6, and 3.1.8. Perishable samples are refrigerated if analysis will be delayed.

3.4.3 The log-in sheet and sample receipt documents are then forwarded to the Log-in Clerk who assigns sample numbers and completes sample log-in through the LIMS. A copy of the log-in sheet is returned to the Group Leader so that sample numbers can be applied to the sample containers.

3.5 RECEIPT OF RADIOACTIVE SAMPLES AND SAMPLES FOR RADIOCHEMISTRY ANALYSIS

This procedure is applicable at LSG facilities possesing a radioactive materials license and/or performing radiochemistry analyses.

3.5.1 Sample Receiving Personnel

a. Examine the documentation received with each sample shipment to determine whether the shipper has identified the samples as containing radioactive materials. If samples are identified as radioactive, handle them as a radioactive

material. Notify the RSOD. Samples will be handled as radioactive materials and be segregated from non-radioactive samples.

b. Check the client and project site name of each sample shipment against the list of clients/projects potentially shipping radioactive materials. (Note: This list is provided by the RSOD and updated as necessary.)

c. Samples that are not identified by the shipper as radioactive and that have not been received from clients on the list described in step 3.5.1b above are considered to be non-radioactive and are handled as such.

3.5.2 Sample Custodians

a. If the samples are not identified as radioactive but have been received from a client on the list described in 3.5.1b above, survey the sample using the uR survey instrument maintained in the receiving area as follows. Note: Surveys are to be performed only by personnel trained by the RSOD.

Also survey all sample containers submitted for radiochemistry analysis so that samples presenting a potential cross-contamination problem can be identified. (Note: bench liner is not required for handling these samples. Gloves are recommended.)

i. Line the lab bench with absorbent paper and wear gloves to handle the samples.

ii. Verify that the uR survey meter is within calibration, i.e., less than six months have passed from the calibration date. If the calibration date is exceeded, return the meter to the RSOD. Obtain another meter for sample screening.

iii. Record the make, model, and calibration date of the meter on the sample survey record (Figure 7-6 or equivalent).

iv. Perform a battery check and record the result. If the battery check fails or degrades over time, notify the RSOD.

v. Turn the scale knob to the lowest scale. Point the meter away from the samples and measure ambient background. Record the value on the survey record.

vi. Place the front end of the meter in contact with the sample to be measured. Record the sample number and the instrument reading on the survey record.

If the needle goes off-scale, select the next highest scale setting. Repeat until the reading comes on-scale. Record this final measurement on the survey record.

b. If a sample reads >1 mR/hr, notify the RSOD immediately. (Notify the Radiochemistry Group Leader in his/her absence.) Do not handle the sample further.

If a sample reads >10X background but <1 mR/hr, place a radioactive materials sticker on the sample and move it to a controlled radiological area for storage. The sample will be handled as a radioactive sample; it will be segregated from nonradioactive samples.

If a sample for radiochemical analysis reads above background but <10X background, label the sample with a colored sticker and write the reading on the sticker. This information will be helpful to radiochemistry lab personnel from an analytical and cross-contamination prevention standpoint.

c. If radioactive samples are received after hours, or when no member of the Radiochemistry Laboratory is available, transfer the samples to the radioactive sample staging area designated by the RSOD.

d. The RSOD will determine the safe handling procedures appropriate to the radioactivity level of the samples as described in Appendix-N.

3.6 RECEIPT OF PERFORMANCE EVALUATION (PE) SAMPLES

3.6.1 Upon receipt, external PE samples are given to the local Quality Assurance Representative (QAR) prior to log-in. (Note: Radiochemistry PE samples from EMSL-LV are radioactive and are handled in accordance with LSG Procedure RS-7.0, Handling and Shipment of Radioactive Materials.) The QAR completes the sample log-in sheet, identifying analytes and tests to be run on each sample. The due date for the completion of analysis is also defined, along with any special requirements. This information is identified on the work list.

3.6.2 The external PE samples are returned to the QAR following log-in. The QAR gives the samples to the Group Leaders along with the preparation instructions and a copy of the report form. Any special requirements are discussed at that time.

3.7 RECEIPT OF SAMPLES DURING OFF-HOURS

3.7.1 The Logistic Support Group Leader makes arrangements for an LSG staff member to receive samples after 5 p.m., on weekends, and on holidays.

3.7.2 The procedure for maintaining chain of custody and sample integrity for off-hours sample receipt is shown in flowchart form on Figure 7-11. Logistic support personnel and other LSG employees working evenings or weekends must follow this procedure.

3.8 BIOASSAY SAMPLES RECEIVED DURING OFF-HOURS

The procedure described above is followed. Bioassay samples are stored in the locked cooler. The shipping documents are placed in the "NOTICE" box on the bioassay laboratory door.

The following working day, bioassay personnel inspect the shipping containers and samples, review the shipping documents, and complete the sample log-in sheet following LSG Procedure QA-7, sections 3.1.2 through 3.1.4.

The log-in sheet and shipping documents are then forwarded to the Log-in Clerk who assigns sample numbers and completes sample log-in through the LIMS. A copy of the log-in sheet is returned to the Group Leader so that sample numbers can be applied to the sample containers.

3.9 SAMPLE STORAGE

3.9.1 As soon as possible after the sample log-in sheet is completed and prior to sample storage, the Sample Custodian verifies the pH of chemically preserved, aqueous samples (except VOA and TOX samples) using broad-range pH paper. The pH check is recorded in a laboratory notebook. If pH adjustment is required, it is performed and documented in the notebook. An NC/CA record is opened and the NC/CA number is documented on the sample log-in sheet under "Anomalies."

3.9.2 The Sample Custodian places the samples in the appropriate storage area. Samples for volatile organics analysis are segregated from other samples to minimize the opportunity for cross-contamination. Samples requiring preservation at 4°C are stored in refrigerated storage units. Organic standards and samples must be stored separately. Samples requiring direct laboratory tracking are maintained in locked storage units.

Sample storage locations for the Houston and Pittsburgh facilities are shown in Tables 7-1 and 7-2, respectively.

3.9.3 Samples are retained in primary storage until work is completed. Samples are retrieved and stored by Sample Custodians or analysts. Following generation of the report, the Sample Custodian moves the samples to secondary storage. Thirty days thereafter, unless otherwise specified, the samples are disposed of in accordance with LSG's waste handling procedures.

3.10 REVIEW OF SAMPLE LOG-IN

3.10.1 Following sample log-in, the laboratory sample log-in sheets, the documents received with each set of samples, and a printout from the LIMS of the information entered at sample log-in are routed to the Project Managers for review of the following.

- Are the correct preparation and analysis methods assigned?
- Is all of the chain-of-custody information in agreement? Has laboratory receipt been documented on the field chain-of-custody record and the air bill?
- Is all sample log-in documentation accounted for?
- Are there any anomalies with sample containers, preservation, or sample identification that the client should be informed of? If any anomalies were noted on the laboratory sample log-in sheet, the Project Manager contacts the client to discuss resolution of the problem. The Project Manager then notes the action to be taken on the nonconformance/corrective action record, which is maintained in the client file, and directs efforts as necessary to carry out the resolution.
- Is pricing correct?
- Are quality control, deliverables, and lab tracking designations correct?
- Have the necessary special instructions been entered.

If any of the information entered into the LIMS is incorrect, the Project Manager notes the appropriate changes on a speed letter (Figure 7-7 or equivalent). The speed letter is distributed to the effected Group Leaders to alert them to error. When the changes have been completed, the Project Manager signs and dates the laboratory sample log-in sheet.

3.10.2 After each Project Manager has reviewed the log-in documents, the laboratory sample log-in sheets, speed letters containing corrections, documents received with the samples, and LIMS printout are forwarded to the Laboratory Operations Coordinator. The LIMS sample receipt and log-in documents are then forwarded to the Sample Log-in Clerk who makes the corrections. Completed corrections are noted on the speed letter and a copy of the speed letter is returned to the Project Manager. The laboratory sample receipt and log-in documents are maintained in the active jobs file.

3.11 SAMPLE ANALYSIS AND DATA ENTRY

3.11.1 Periodically, the Group Leader prints a work list from the LIMS. The work list shows the sample number, date sampled, date received, preparation method, analytical method, analytes, client, and special instructions for the selected test(s) and samples. As soon as sample log-in is completed, the analyses are available for inclusion on the work list.

3.11.2 Working from the work list, immediate work sheet, or short holding time parameters work sheet, the analyst requests the appropriate samples from the Sample Custodian. If the analyst is working during a weekend or evening when a Sample Custodian is not available, the analyst will retrieve the samples.

3.11.3 Sample preparation and analysis is documented in laboratory notebooks and /or on preprinted worksheets. In addition, instrument output (chromatograms, quantitation reports, etc.) are printed and retained in files in the laboratory. (See also LSG Procedure QA-10, section 3.1.1.)

Samples are identified by their full sample number (alpha and numeric characters) on the log books or preprinted sheets. Sample identifications may be abbreviated or omitted on instrument printouts if necessary due to data system

limitations. They must be correlated with the file name on the analysis log, and the full file name shown on the instrument printout.

During sample processing, the last four digits of the sample number, at a minimum, are transferred to temporary sample containers such as beakers, flasks, or vials. Final sample storage containers for distillates, digestates, extracts, etc. are labelled with the full sample number.

3.11.4 During data entry, the book and page number of the analysis log record is entered into the LIMS along with the results so that the raw data are easily retrievable. The process of data entry is outlined in LSG Procedure AP-003, Program Guide for LSG's Laboratory Information management System (LIMS).

3.12 REPORT PREPARATION

3.12.1 Following review and approval of the data at the Laboratory Group Leader and Laboratory Manager levels, the project deliverables are assembled. LSG's standard lab analysis report, which is generated through the LIMS, is shown in Figure 7-8. This report may be supplemented by a quality control report, which contains the following supplementary information, as applicable to the analytes in the report.

- Sample preparation method, batch number, date, time, and analyst.
- Sample analysis method, batch number (if not previously assigned during sample preparation), date, time, analyst, and instrument.
- Surrogate standard recovery for organic parameters, by fraction.
- Laboratory control sample recovery for parameters for which surrogate standards are not feasible.

- Method blank results.
- Duplicate and matrix spike or duplicate matrix spike results.

The original copy of the field chain-of-custody record is also delivered with the report, unless it has been previously returned to the client.

The lab analysis report and quality control report may be supplemented with additional information, such as initial and continuing calibration data or raw data, at the client's request. This information is assembled manually.

LSG will also prepare full USEPA CLP deliverables for work performed according to CLP protocols.

3.12.2 A complete set of deliverables is given to the Project Manager. He/she reviews the final report for completeness and clarity. If acceptable, the Project Manager authorizes delivery of the package to the client. If unacceptable, corrections/clarifications are made to the report as required.

A copy of all deliverables, the laboratory sample log-in sheet, and documents received with the samples are retained in the client or project files.

3.13 BIOASSAY REPORT PREPARATION

3.13.1 Upon completion of analysis, the analyst, date and time of analysis, results, and book and page number are entered into the LIMS.

3.13.2 Bioassay personnel prepare the laboratory analysis report containing the information listed in Table 7-3.

3.13.3 The report is reviewed and approved (signed) by the Bioassay Group Leader and a Quality Assurance Representative prior to its delivery to the client.

3.14 CLIENT AND PROJECT FILES

The client files contain the following for each job. (Note: All records will not be applicable to all jobs.)

- Bill of lading/air bill
- Field chain-of-custody records
- Sample log-in sheet (and immediate worksheet when generated)
- Sample tags
- All project-related correspondence (internal and external)
- Laboratory tracking records
- A complete set of the deliverables
- Holding blank data

For CLP projects, these records plus a document inventory (see Figure 7-9) and all raw data (i.e., laboratory notebook pages, preprinted work sheets, and instrument printouts) will be retained in separate, project-specific files. The Document Custodian will maintain a document inventory for each project file.

3.15 SAMPLE TRACKING

3.15.1 Indirect Tracking

The handling of all samples may be traced indirectly through the following documents:

- Field chain-of-custody record (when supplied by the client) showing custody of samples from the time of collection through their receipt at the laboratory. Samples are identified by a field/client identification.

- Sample log-in sheet documenting date/time of sample receipt, custody information received with samples (seals, records, tags), condition of samples upon receipt. Field/client sample identification is listed and correlated with a unique laboratory tracking number. Anomalies with sample integrity (physical or chain of custody) are identified.

- Analysis logs documenting the date and time of sample preparation and/or analysis, the analyst, the method used, the instruments used, etc. Each result reported is traceable to an analysis log entry. Whenever practical, the logs are supplemented by instrument output, such as quantitation reports, chromatograms, etc..

- The laboratory analysis report, which lists results for the samples. This may be supplemented by a quality control report, which provides the additional information listed above, or it may be replaced by a CLP data package.

3.15.2 Direct Tracking

The National Enforcement Investigations Center (NEIC) of the EPA defines custody of evidence in the following ways:

- It is in your actual possession, or

- It is in your view after being in your physical possession, or

- It is in your possession and then you locked or sealed it to prevent tampering, or

- It is in a secure area.

LSG will maintain direct sample tracking showing the transfer of samples from secure, locked sample storage to the secure laboratory area and back to locked storage upon client request.

To maintain direct chain of custody within the laboratory, samples, sample extractions, and sample digestions are stored in locked areas when not in use for sample preparation or analysis. Keys to the locked storage areas are controlled by the Sample Custodian or designated laboratory personnel. The following LSG personnel are authorized to access samples in locked storage.

- Project Managers
- Drivers
- Laboratory Analysts
- Laboratory Assistants
- Laboratory Group Leaders and Assistant Group Leaders
- Laboratory Managers
- Logistic Support Group Leaders
- Quality Assurance Personnel
- Sample Custodians
- Sample Log-in Clerks

The following steps are taken to document the location of the samples at all times.

- Transfer of samples between logistic support personnel for the purposes of pH checks and sample storage are documented on the upper right-hand corner of the Laboratory tracking record (Figure 7-4).

- When a sample is to be placed in locked storage following check-in, or a sample extract or a sample digestion is to be placed in storage following sample preparation, the Sample Custodian, Log-in Clerk or analyst obtains a key to the locked storage area and completes the lab tracking record, signing the "Returned to Storage" section. The storage area is unlocked, and the sample or sample preparation is placed in the designated area. The storage unit is locked immediately, and the key is returned.

- When a sample (or its extract or digestion) is to be removed from storage, the Sample Custodian or analyst obtains a key to the storage area, completes the lab tracking record, and unlocks the storage area to permit removal of the sample. The storage area is locked immediately after the removal of the sample, and the key is returned. If the sample is transferred from a Sample Custodian to an analyst, the transfer is documented using the "Transferred to" box next to the "Removed from Storage By" box. The analyst is now responsible for the custody of sample.

- When a sample (or its extract or digestion) is to be returned to locked storage by an analyst, he/she obtains a key to the storage area, signs the "Returned to Storage" box of the lab tracking record, and unlocks the storage area to permit return of the sample. The storage area is locked immediately after return of the sample, and the key is returned.

  When a sample, extract, digestate is transferred to a Sample Custodian for return to locked storage, the transfer is documented as well as the return to storage using the last two right-hand boxes of the record. The storage area is locked immediately after returning of the sample, and the key is returned.

When the deliverables for a project with direct tracking are forwarded to the Project Manager, he/she informs Data Management of the project name, sample numbers, and categories of analytes (i.e., VOA, BNA, metals, inorganics, etc.). Data management personnel then collect the lab tracking records, verify them against the data package for accuracy, and file them in the client file or project file.

3.16 INTERFACILITY SAMPLE SHIPMENTS

In order to use its analytical resources most efficiently and maximize sample throughput, LSG may ship samples from one facility to another for analysis as contractual and regulatory restrictions permit. Since both fixed-base laboratories operate under this General Quality Assurance Plan, the results obtained and level of services rendered at either facility are comparable.

3.16.1 Decision Making

The Operations Coordinator at the originating facility (or the Logistic Support Group Leader in his/her absence), in conjunction with the Group Leaders and Project Managers, selects possible samples that might be processed more efficiently at the sister facility because of additional laboratory capacity. Note: Where contractual or regulatory restrictions

require that samples be analyzed at the originating facility, interfacility shipments will not be considered.

The Operations Coordinator at the originating laboratory contacts the Operations Coordinator at the receiving laboratory to discuss the feasibility of forwarding the selected samples for analysis. The analyses required, sample matrices, any restrictions on the analytical method employed, any anticipated sample matrix-related problems, and quality control, deliverables, and turnaround requirements are also discussed. Project Managers are consulted to determine explicit project requirements. If the Operations Coordinators are unable to agree on the interfacility sample shipment, the Laboratory Managers are consulted.

3.16.2 Project Training

If a project plan or QA plan was prepared for the job, the plan will be distributed and training conducted at the receiving laboratory by the Project Manager.

3.16.3 Sample Shipment

The Operations Coordinator at the originating facility identifies the appropriate sample container for the parameter(s) of interest (e.g., wet chemistry bottle, organics bottle, cyanide bottle) and the necessary sample volume. Preferentially, the entire sample will be sent; however, an extract and/or a digestate may be sent, or an aliquot of a sample, extract, or digestate may be sent, depending on the work to be done at the originating laboratory, however. The Operations Coordinator completes an interfacility sample shipment form (Figure 7-10).

The Interfacility Sample Shipment Form is then forwarded to the Logistic Support Group Leader, who assembles the samples for shipment. (This task may be delegated to a Sample Custodian as long as explicit instructions are provided.) When extracts or digestates are included in a

shipment, their related quality control checks (e.g., method blanks, lab control standards, duplicates, matrix spikes, MS/MSDs) must also be sent in the shipment for analysis by the receiving laboratory.

Once the samples have been assembled, the Operations Coordinator verifies that all of the requested samples (and associated quality control check samples for extracts and digestates) have been assembled. A Sample Custodian then packs the samples in a manner that will prevent leaking or breakage, and retain temperature control if required for any of the analytes. The mode of transportation and transfer of custody to the carrier are listed on the Interfacility Sample Shipment Form and a copy of the form is put into a plastic bag and placed in the shipping container. The shipping container is then sealed with custody seals such that the seals will break should the container be opened. A copy of the Interfacility Sample Shipment Form is also forwarded to the Operations Coordinator at the originating laboratory.

3.16.4 Sample Receipt

Upon receipt of the sample shipment, the samples are logged-in according to standard procedure. The Operations Coordinator at the receiving facility functions as the Project Manager for interfacility work, reviewing log-in, deliverables, and invoices, and resolving any anomalies or problems encountered with the Operations Coordinator at the originating facility.

Following log-in review, the receiving laboratory's Operations Coordinator returns a copy of the completed chain-of-custody record and sample shipment form to the originating laboratory's Operations Coordinator.

3.16.5 Reporting

As sample preparation and analysis is completed, the data is entered into the receiving laboratory LIMS and the originating laboratory LIMS by receiving laboratory personnel.

The originating laboratory generates and delivers the reports to the clients as described previously in this procedure. The receiving laboratory delivers their report and invoice to the originating laboratory Operations Coordinator. He/she verifies the invoice and files the report.

3.17 SAMPLE SHIPMENT TO CLIENTS, SUBCONTRACTORS

Paragraph 3.16.3 is followed except that a chain-of-custody record rather than an interfacility sample shipment record is sent with the samples, along with a cover letter explaining the analysis request in detail: tests, analytes, and deliverables, at a minimum.

4.0 RECORDS

The contents of the client and project files will be retained in the client file or case file in support of this procedure, in accordance with LSG Procedure QA-20 of this General QA Plan.

Figure 7-1
Sample Log-in Sheet

SAMPLE LOG-IN SHEET
HALLIBURTON NUS LABORATORY SERVICES GROUP

Page _____ of _____

Client: _____ ☐ Check if new Client
Report Address: _____
_____
Attention: _____
CC: _____
Phone: _____

Project: _____
Invoice Address: _____
_____
_____
Attention: _____
Phone: _____

Date/Time Sample Receipt: _____
Air Bill No.: _____
No. Coolers Received: _____
Custody Seals: Yes / No Intact: Yes / No
Custody Seals No.: _____
Chain-of-Custody Record: Yes / No
Sample Tags: Yes / No

Log-In Date:	Client No.:	Job No.	SIC	Price Date:	Discount (%) List Premium (%)	PO No.:	Vendor No.:	Work Order No.:	Project No/ PMS Code:

Condition of Samples Upon Receipt:
Ice: Yes / No Ice Packs: Yes / No
Containers Intact: Yes / No
Other: _____

Anomalies: _____

Change Order: Yes / No
Deletions: _____
Additions: _____

Proposal No.: _____

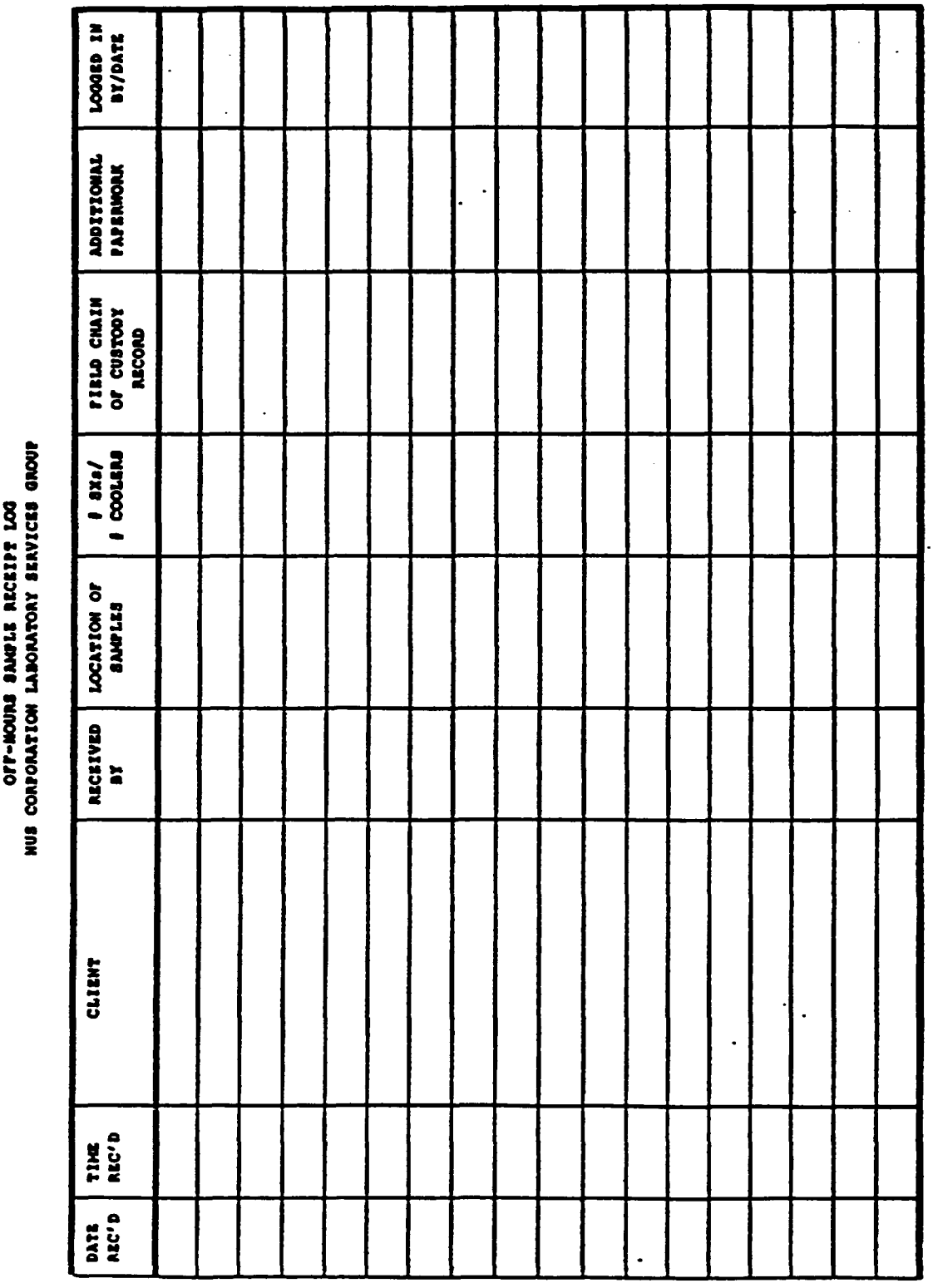
Task No.	Lab Sample Number	Matrix	Sample Identification	Date Sampled	Test Codes (AM/PM)	Bottles

Special Instructions: _____

Special Requirements:
___ CLP ___ MBIS
___ Lab Tracking ___ QC Report
___ Labor ___ Add. Deliverables

Project Manager: _____
Written up by: _____
Logged-in by: _____
Reviewed by: _____

Figure 7-2
Off-Hours Sample Receipt Log



OFF-HOURS SAMPLE RECEIPT LOG
NUS CORPORATION LABORATORY SERVICES GROUP

DATE REC'D	TIME REC'D	CLIENT	RECEIVED BY	LOCATION OF SAMPLES	# SKs/ # COOLERS	FIELD CHAIN OF CUSTODY RECORD	ADDITIONAL PAPERWORK	LOGGED IN BY/DATE

Figure 7-3
Short Holding Time Parameters Work Sheet

SHORT HOLDING TIME PARAMETERS WORKSHEET
NUS CORPORATION LABORATORY SERVICES GROUP

Date/Time Received _____ SAMPLE NUMBERS
Sample No.

Parameters	Holding Time																
BOD	48 Hrs.																
Chlorine, Free Residual	Immed.																
Chlorine, Total Residual	Immed.																
Chromium, Hexavalent	24 Hrs.																
Coliform, Fecal	30 Hrs.																
Coliform Total	30 Hrs.																
Color	48 Hrs.																
Iodide	24 Hrs.																
Iron, Ferrous	Immed.																
MBAS	48 Hrs.																
Nitrate (unpres.)	48 Hrs.																
Nitrite	48 Hrs.																
Odor	24 Hrs.																
Orthophosphate	48 Hrs.																
Oxygen, Dissolved	Immed.																
pH	Immed.																
pH HSL																	
Phosphorous, Hydrolyzable	48 Hrs.																
Phosphorous, Total Dissolved	24 Hrs.																
Solids, Total Dissolved	48 Hrs.																
Solids, Setteable	48 Hrs.																
Sulfite	Immed.																
Turbidity	48 Hrs.																

LABORATORY TRACKING RECORD
HALLIBURTON NUS LABORATORY SERVICES GROUP

PAGE _____ OF _____

Sample Storage Location: _____

Case No./Project Name: _____

SDG Designation: _____

Samples Received by: _____
Date / Time *

Samples Transferred to: _____
Date / Time *

Sample Numbers	Sample Containers
_____	_____
_____	_____
_____	_____
_____	_____

Container/ Fraction	Lab Sample Numbers (including QC samples)	Removed from Storage			Transferred			Transferred			Returned to Storage		
		By	Date	Time*	To	Date	Time*	From	Date	Time*	By	Date	Time*

* Use military time (i.e., 0145 = 1:45 a.m.; 1345 = 1:45 p.m.).

Figure 7-4
Laboratory Tracking Record

Figure 7-5
Immediate Work Sheet

IMMEDIATE WORKSHEET
RUS CORPORATION LABORATORY SERVICES GROUP

DATE/TIME RECEIVED _____ CASE/PROJECT NAME _____

RUS Sample No.	EPA/Client Sample No.	Matrix	Analyses	Special Instructions

DISTRIBUTION:

SAMPLE SURVEY RECORD

HALLIBURTON NUS LABORATORY SERVICES GROUP

Page _____ of _____

Date: _____

By: _____

Reviewed By: _____

Survey Type: Meter: _____
Smear: _____
Leak Test: _____

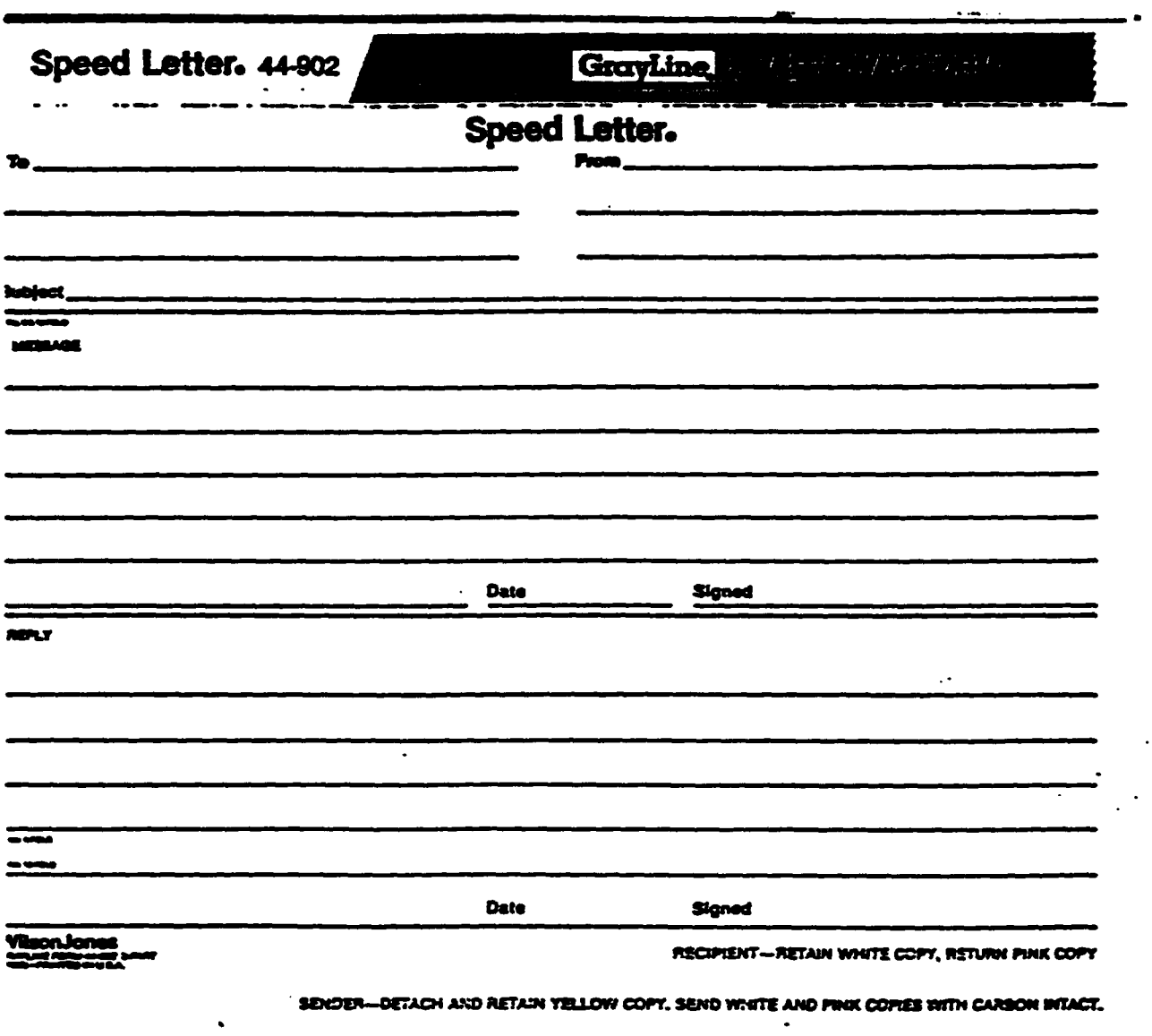
Survey Instrument:
Manufacturer: _____
Model Number: _____
Serial Number: _____
Calib. Date:

Battery Check: _____
Background (µR/hr): _____

SAMPLE NUMBER(S)	INSTRUMENT READING (µR/hr)	REMARKS

Figure 7-6
Survey Record

Figure 7-7
Speed Letter



Speed Letter. 44-902 GrayLine

Speed Letter.

To _____ From _____

Subject _____

MESSAGE

Date Signed

REPLY

Date Signed

Vilson Jones

RECIPIENT—RETAIN WHITE COPY, RETURN PINK COPY

SENDER—DETACH AND RETAIN YELLOW COPY. SEND WHITE AND PINK COPIES WITH CARBON INTACT.

Figure 7-8
Lab Analysis Report

NUS CORPORATION

Laboratory Services Group
2300 Campbells Run Road
Pittsburgh, PA 15205

REMIT TO:
Park West Two
Cliff Mine Road
Pittsburgh, PA 15275
412-788-1080

1.

LABORATORY ANALYSIS REPORT

CLIENT NAME: NUS CORPORATION
ADDRESS: 2300 CAMPBELLS RUN ROAD
PITTSBURGH, PA 15205-0000
ATTENTION: MS. LISA HARDING

NUS CLIENT NO: 0157 0002
VENDOR NO:
WORK ORDER NO: 23020
REPORT DATE: 02/07/89

SAMPLE IDENTIFICATION: LEACHATE BLANK - BATCH 357
NUS SAMPLE NO: P0108244
DATE SAMPLED :
DATE RECEIVED: 19-JAN-89
APPROVED BY: Joanne C. Siemaic

TEST	DETERMINATION	RESULT	UNIT
8VOA	VOLATILES - ZHE - PART 261		
	1,1,1,2-Tetrachloroethane	(5	ug/L
	1,1,1-Trichloroethane	(5	ug/L
	1,1,2,2-Tetrachloroethane	(5	ug/L
	1,1,2-trichloroethane	(5	ug/L
	1,1-Dichloroethylene	(5	ug/L
	1,2-Dichloroethane	(5	ug/L
	2-Butanone (MEK)	(10	ug/L
	Acrylonitrile	(100	ug/L
	Benzene	(5	ug/L
	Carbon Tetrachloride	(5	ug/L
	Carbondisulfide	(5	ug/L
	Chlorobenzene	(5	ug/L
	Chloroform	(5	ug/L
	Methylene Chloride	(5	ug/L
	Tetrachloroethylene (Perchlors)	(5	ug/L
	Toluene	(5	ug/L
	Trichloroethylene	(5	ug/L
	Vinyl Chloride	(10	ug/L
	i-Butanol	0	ug/L

COMMENTS: "U" indicates that the compound was undetected after a library search for ions characteristic for this compound.

Figure 7-9
Document Inventory

(NOTE: XXXXX = Case Number)

RETURN TO:

NUS CORPORATION
5350 Campbells Run Road
Pittsburgh, PA 15205

Attn:

DOCUMENT RECEIPT ACKNOWLEDGEMENT

The following documents were received from the NUS Corporation, Laboratory Services Division.

Received By: _____
Signature

_____
Title

_____
Date

DOCUMENT CONTROL NUMBER	DOCUMENT(S)	NUMBER OF PAGES
XXXXX-3-0001	Document Inventory	1
XXXXX-3-0002	Bill of Lading	2
XXXXX-3-0003	Chain of Custody Record	4
XXXXX-3-0004	SMO Traffic Report	1
XXXXX-3-0005	Sample Tags (37 Tags)	1 (envelope)
XXXXX-3-0006	Sample Log-In Sheet	1
XXXXX-3-0007	Auxiliary Sheet	1
XXXXX-3-0008	Immediate Work Sheet	1
XXXXX-3-0009	SDG Cover Sheet	1
XXXXX-3-0010	Correspondence	1
XXXXX-3-0011	CCS Report/Response	47
XXXXX-3-0012	Laboratory Analysis Report	60
XXXXX-3-0013	Laboratory Tracing Record	6
XXXXX-3-0014	Holding Blank Data	12
XXXXX-3-0015	Sample Preparation Notebook Page	4
XXXXX-3-0016	Injection Log Notebook Pages	11
XXXXX-3-0017	Original GC Chromatograms	21
XXXXX-3-0018	Data Package	818

Figure 7-10
Interfacility Sample Shipment Form

INTERFACILITY SAMPLE SHIPMENT AND CHAIN-OF-CUSTODY RECORD
NUS CORPORATION LABORATORY SERVICES GROUP

Receiving Lab: _____ Originating Lab: _____

Shipment Approved by: _____ Attention: _____

Date Shipped: _____ Carrier: _____ Total Number of Bottles in Shipment: _____

QC Requirements: _____ Standard; _____ Other: _____
Deliverables: _____ Standard; _____ Other: _____

NOTE: Reference our client number and name for each sample on our 9903 report.

Orig. Lab Number/ Field ID	Rec. Lab Number	Client	Client No.	Pricing	Charge No.	Date Sampled	Bottles	Tests	Due Date

Relinquished by: _____ Date/Time _____ Received by: _____ Date/Time _____

Air Bill No. _____

Additional Instructions: _____ Page _____ of _____

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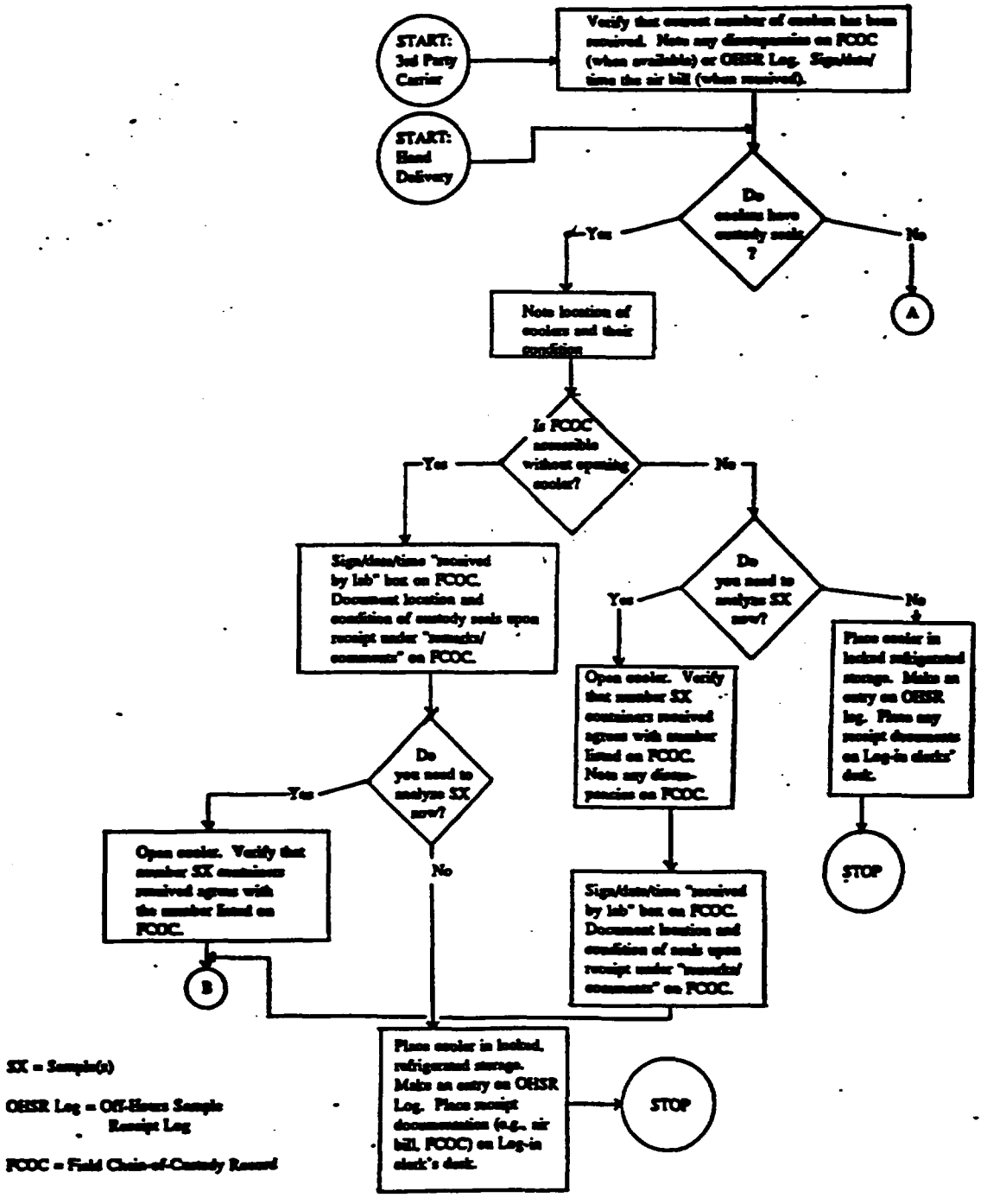
Off-Hours Sample Receipt Flowchart



Off Hours Sample Receipt Flowchart (Continued)

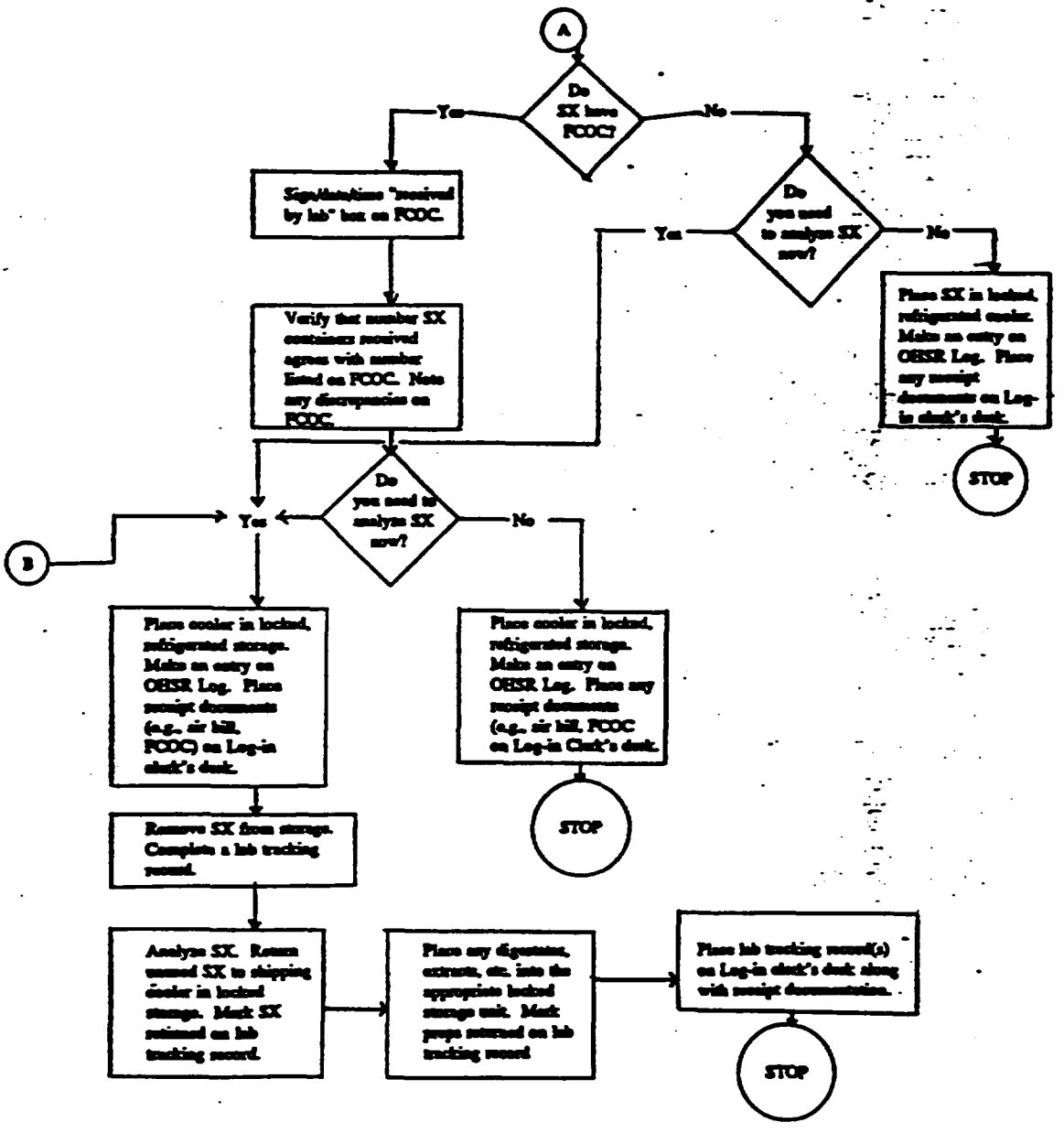


TABLE 7-1

SAMPLE STORAGE LOCATIONS
HOUSTON LABORATORY

SAMPLE STORAGE LOCATION	SAMPLE TRACKING	TYPES OF SAMPLES STORED THERE
Walk-in coolers off sample receiving area	Indirect Tracking	Aqueous extractable organics (as received); Aqueous inorganics; Soils and wastes (except volatiles.
3-Door cooler on loading dock	Indirect Tracking	Volatiles, aqueous and nonaqueous
Walk-in cooler off inorganic lab	Direct Tracking	All samples except VOAs, metals, and organic extracts
Locked Kenmore Refrigerator in GC/MS lab	Direct Tracking	Volatiles, aqueous and nonaqueous
Locked freezer in GC/MS maintenance area	Direct and Indirect Tracking	BNA Extracts
Admiral refrigerator in GC/MS lab	Indirect Tracking	VOAs in progress
Kelvinator refrigerator in GC/MS	Indirect Tracking	VOAs in progress
Kelvinator refrigerator in GC lab	Indirect Tracking	VOAs in progress
Locked, refrigerator in GC lab	Direct and Indirect Tracking	Organic extracts
Room off sample receiving	Indirect Tracking	Metals samples
Metals lab	Indirect Tracking	Metals digestates

TABLE 7-1
(CONTINUED)

SAMPLE STORAGE LOCATION	SAMPLE TRACKING	TYPES OF SAMPLES STORED THERE
Locked room off loading dock	Direct Tracking	Metals samples and digestates
Bioassay lab	Indirect Tracking	Bioassay samples Note: If these must be stored overnight prior to test initiation, they are stored in the walk-in coolers off the sample receiving area.

TABLE 7-2

SAMPLE STORAGE LOCATIONS
PITTSBURGH LABORATORY

SAMPLE STORAGE LOCATION	SAMPLE TRACKING	TYPES OF SAMPLE STORED THERE
New walk-in cooler (locked)	Direct and Indirect	All nonradioactive samples and sample preparations, except VOAs and metals digestates
Old walk-in cooler (locked)	Direct and Indirect	All radioactive samples and sample preparations except VOAs
3-Door Cooler (locked)	Direct and Indirect	All VOA samples
Warehouse cage (locked)	Direct	Metals digestates
Metals lab	Indirect	Metals digestates
Admiral refrigerator in GC/MS lab (locked)	Direct and Indirect	BNA extracts
White refrigerator in GC lab	Indirect	Extracts for GC analysis
Brown refrigerator in GC lab (locked)	Direct	Extracts for GC analysis

TABLE 7-3
Content of Bioassay Laboratory Analysis Reports

Introduction

1. Permit number
2. Toxicity testing requirement of permit
3. Plant location
4. Name of receiving body of water
5. NUS Corporation laboratory name, address, and phone number

Source of Effluent and Dilution Water

1. Effluent Samples
   - Sampling point
   - Collection dates and times
   - Sample collection method
   - Physical and chemical data
2. Surface Water Samples (if used as test sample)
   - Sampling point
   - Collection of dates and times
   - Sample collection method
   - Physical and chemical data
3. Dilution Water Samples
   - Source
   - Collection date and time
   - Pretreatment
   - Physical and chemical characteristics

Test Methods

1. Toxicity test method used
2. End point(s) of test
3. Deviation(s) from reference method, if any, and the reason

TABLE 7-3
Content of Bioassay Laboratory Analysis Reports

Test Methods (Continued)

4. Date and time test started
5. Date and time test terminated
6. Type of test chambers
7. Volume of solution used per chamber
8. Number or organisms per test chamber
9. Number of replicate test chambers per treatment
10. Acclimation of test organisms (temperature and salinity mean and range)
11. Test temperature (mean and range)
12. Specify if aeration was needed

Test Organisms

1. Scientific name
2. Age
3. Life stage
4. Source

Information on mean length and weight, diseases and treatments, and the taxonomic key used for species identification are documented and retained by LSG.

Quality Assurance

1. Standard toxicant used and its source
2. Date and time of most recent test
3. Dilution water used
4. Results (LC50 or, where applicable, NOEC and/or ECI)
5. Physical and chemical methods used

TABLE 7-3
Content of Bioassay Laboratory Analysis Reports

Results

1. Raw biological data in tabular form, including daily records of affected organisms in each concentration (including controls) and plots of toxicity data
2. Table of LC50's, NOEC's, LOEC's, etc.
3. Statistical methods used to calculate end points
4. Summary table of physical and chemical data
5. Table of quality control data

CORRECTIVE ACTION

1.0 PURPOSE AND APPLICABILITY

This procedure describes the mechanisms by which corrective actions for nonconformances detected through routine sampling and laboratory operations, performance audits, or systems audits are identified and closed. This procedure is applicable to all LSG operations. It interfaces directly with the following LSG Procedures.

- QA-7, Laboratory Sample Custody
- QA-8, Laboratory Quality Control
- QA-10, Data Handling
- QA-11, Systems Audits
- QA-12, Performance Audits

The nonconformance/corrective action record described in this procedure is a tool by which problems and their consequences, and corrective action measures and their outcomes are documented and communicated. They are also used for quarterly Pareto analysis.

2.0 RESPONSIBILITIES

2.1 MANAGERS, GROUP LEADERS, AND FIELD SUPERVISORS

The Laboratory Managers, Field Operations Manager, Group Leaders, Project Managers, and Field Supervisors determine appropriate measures to correct nonconformances identified during routine laboratory operations and systems audits, and are responsible for implementing these actions and for providing feedback to the Quality Assurance Department on progress of corrective actions.

2.2 QUALITY ASSURANCE DEPARTMENT

The Quality Assurance Department (QAD) performs follow-up activities to ensure that any corrective action is implemented, and effective in resolving the nonconformances.

3.0 PROCEDURE

3.1 CORRECTIVE ACTIONS FOR NONCONFORMANCES IDENTIFIED DURING ROUTINE LABORATORY OPERATIONS

Nonconformances can occur at any time during routine laboratory operations – during sample bottle preparation, sample receipt, sample analysis, data reduction, and reporting. When a nonconformance is immediately correctable (i.e., fully correctable by the person identifying the nonconformance within the same work shift), corrective action need only be documented through the records routinely generated for that activity. However, when corrective action cannot be completed by the person identifying the nonconformance within the same work shift, a nonconformance/corrective action (NC/CA) record, Figure 15-1 for Sample Control or Figure 15-2 for Sample Analysis is completed.

Performance audits evaluate the end product of a process or series of processes. If the end product is acceptable, the process is assumed to be acceptable. However, if the end product is unacceptable, the process must be examined thoroughly to determine the cause(s) of the failure and correct them. A nonconformance/corrective action record is opened for each performance evaluation sample failure to document the failure and track investigation and correction of the problem.

3.1.1 Sample Control Nonconformances

a. Sample control NC/CA records are used to document and track resolution of the following nonconformances:

- Chain of custody
- Broken sample container
- Incompatible sample container or cap
- Incorrect sample pH

- Incorrect temperature preservation
- Headspace in VOA vials or TOX bottles (aqueous samples)
- Missed hold time
- Insufficient information available to log-in samples

b. Sample control NC/CA records are prenumbered as follows:

SC-XX-YYYY

Where XX is the last two digits of the year and YYYY is a consecutive number starting with 0001. The records are maintained in a 3-ring binder in sample receiving. Completed records are periodically forwarded to the QA files.

c. When a sample control nonconformance occurs, the person identifying the nonconformance:

i. Completes Section 1 of the next available, sequentially numbered record.

ii. Records the NC/CA number on the sample log-in sheet under "Anomalies," if the nonconformance is identified during sample receipt inspection.

iii. Forwards the original to the project manager for the job, retains a copy in the binder, and copies anyone else who should be informed of the problem.

NOTE: "Corrective measures" in section 1 is completed by whomever takes corrective steps -- the originator, Project Manager, or someone else.

The Project Manager:

i. Completes Section 2 of the NC/CA record and contacts the client when appropriate. If the client is contacted (e.g., to discuss whether or not resampling will be performed) the specific person contacted, and the date are documented on the record.

NOTE: If there is any problem with sample integrity (e.g., preservation, sample container, hold time, chain-of-custody) the client must be contacted to allow him/her to decide appropriate corrective action.

ii. Initiates any corrective actions.

iii. Once the problem is resolved to the client's satisfaction (or to the extent possible), the Project Manager:

i. Returns the original form to the binder; the copy is discarded.

ii. Provides a copy of the record to anyone else who should be informed of the nonconformance and its resolution.

d. QAD reviews open NC/CA records and tallies nonconformances during periodic inspection of logistic support and customer services work groups, and completes Section 3 of the original record.

3.1.2 Sample Analysis Nonconformances

a. Sample analysis NC/CA records are used to document and track resolution of the following nonconformances:

- Failure to perform the required quality control checks
- Failure to meet calibration or quality control criteria

NOTE: This includes any out of control occurrence on control charts. Cross reference the NC/CA number on the control chart to enhance traceability of corrective action.

- Error in data reduction or reporting.
- Unusual sample response during analysis that is likely to adversely affect the results or precludes completion of analysis.

b. Sample analysis NC/CA records are prenumbered as follows:

SA - Z - XX - XXXX

Where Z is the department code of the analysis laboratory (as opposed to the sample preparation laboratory), XX is the last two digits of the year, and YYYY is a sequential number starting with 0001.

The forms are maintained in a 3-ring binder in the analysis lab.

c. When a sample analysis nonconformance occurs, the person identifying the nonconformance:

i. Completes Section 1 of the next available, sequentially numbered record from his/her work group.

NOTE: "Corrective measures" in section 1 is completed by whomever takes corrective steps--the originator, another analyst, or someone else.

ii. Forwards the record to the Group Leader of the work group that will take the corrective action, and places a copy in the binder. (If corrective action will be taken in the originator's work group, the original can remain in the binder.)

iii. References the NC/CA number in the raw data and on the proper control chart.

The Group Leader (or designee):

i. Reviews corrective actions, and concurs or requests further actions.

ii. Ensures that the action is implemented.

iii. Completes Section 2 of the NC/CA record.

Upon resolution of the problem, the Group leader:

i. Returns the NC/CA record to the binder; the copy is discarded.

ii. Forwards a copy of the NC/CA record to the Project Manager if the nonconformance cannot be fully rectified (e.g., prep or analysis hold time violated, reanalysis cannot be performed, turnaround time requirement cannot be met).

d. QAD reviews open NC/CA records and tallies nonconformances during periodic inspection of each work group, and completes Section 3 of original record.

3.1.3 Performance Evaluation (PE) Nonconformances

a. Performance sample NC/CA records are used to document and track resolution of performance evaluation failures.

b. Performance evaluation NC/CA records are prenumbered as follows:

PE - Z - XX - YYYY

Where Z, XX, and YYYY are as defined above in 3.1.2b.

c. QAD initiates a record for each internal or external PE failure by completing Section 1 of the next available, sequentially numbered record.

He/she forwards the original to the appropriate Group Leader and retains a copy in the binder.

Group Leader determines root cause and corrective action, completes Section 2 of the record, and returns the record to the QAD within the specified timeframe.

QAD reviews response, accepts the response if complete or requests further investigation. Once the response is accepted, the QAD files original and discards copy in binder.

QAD reviews open records and tallies root causes during periodic inspection of each work group, and completes Section 3 of original record.

3.1.4 NC/CA Trends

In quarterly reports and lab profiles the QAD discusses favorable and unfavorable trends evident from the nonconformances and corrective actions reported.

3.2 CORRECTIVE ACTIONS FOR SYSTEMS AUDIT FINDINGS

3.2.1 Internal Systems Audits

Findings identified through internal systems audits are documented in the lab profile report. During the report review meeting, the Group Leader is asked to acknowledge the need for corrective action and to provide a corrective action commitment date. (See Figure 15-4.) Root cause and specific corrective measures are discussed during the meeting.

The QA Coordinator or Representative opens a follow-up form (Figure 15-5) for each finding. The form is filed with the profile report. During subsequent follow-up, the QA Coordinator or QA

Representative (QAC/QAR) documents the status of corrective actions in section two.

- If the corrective measures taken were effective, the finding is closed in section three and a copy of the closed form is forwarded to the Group Leader.

- If corrective actions have been ineffective or have not been taken, this is noted on the form. The Group Leader must provide a corrective action plan by completing the back of the form. Failure to take effective action thereafter results in the opening of a quality notice.

Open findings are also discussed in the quarterly QA report to management.

A quality notice (QN, Figure 15-6) is opened for chronic nonconformances. The QA Representative adds the notice to the QN log, completes the front of the form, and discusses the nature of the problem with the Lab Manager. The Lab Manager documents his/her concurrence with the need for corrective measures at the bottom of the page. The QAC/QAR then reviews the notice with the Group Leader, who must document root cause, corrective actions, preclusive actions, and completion dates within three working days. Corrective actions must be completed as soon as possible. The notice is filed with the profile report and included in QAD follow-up.

3.2.2 External Systems Audits

The QAC/QAR assigned to the audit and the Laboratory Manager review each audit summary and, once received, the audit report. They determine who within LSG will be tasked with responding to each finding and recommendation, and with directing corrective actions. The QAC/QAR coordinates preparation of the formal audit response and opens a follow up form (Figure 15-5) for each finding or recommendation to track corrective action. The QAC/QAR then follows-up on corrective actions as described for internal audits in section 3.2.1 above.

The status of the audit response and corrective actions are discussed in the quarterly QA report to management.

4.0 RECORDS

The following records are maintained in support of this procedure in accordance with LSG Procedure QA-20, Quality Assurance Records.

- Nonconformance/corrective action records.
- Lab profile report files including follow-up forms/quality notices.
- External audit files including follow-up forms/quality notices.
- Quality notice log.

Figure 15-1

NC/CA # SC-92-

Halliburton NUS Environmental Corporation - Laboratory Services Group
NONCONFORMANCE/CORRECTIVE ACTION RECORD - SAMPLE CONTROL

SECTION 1 : ORIGINATOR

Date/Time: _____

Sample Number(s): _____

Client: _____

Indicate the nonconforming condition(s): _____

_____

_____

_____

Corrective measures : _____

_____

_____

Reported by: _____ Date: _____

FORWARD ORIGINAL TO ACCOUNT EXECUTIVE / PROJECT MANAGER
RETAIN COPY IN NC/CA LOG BOOK • REFERENCE NC/CA # ON LOG-IN SHEET

SECTION 2 : ACCOUNT EXEC. / PROJECT MANAGER

Comments or recommendations: _____

_____

_____

Date corrective action completed: _____

Approved by: _____ Date: _____

RETURN ORIGINAL TO LOGISTICS NC/CA LOG BOOK
FORWARD COPIES, AS APPROPRIATE, TO : _____

SECTION 3 : QA DEPARTMENT

Corrective action satisfactory? ____Yes ____No

Comments: _____

_____

_____

NC/CA closed by: _____ Date: _____

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Figure 15-2

NC/CA # SA-A-92-

Halliburton NUS Environmental Corporation - Laboratory Services Group
NONCONFORMANCE/CORRECTIVE ACTION RECORD - SAMPLE ANALYSIS

SECTION 1 : ORIGINATOR

Date/Time: _____

Analyst: _____ Instrument: _____ Sample #: _____

Dept: _____ Bk. & Pg. #: _____ Client: _____

Test: _____ Prep Analyst: _____ Prep Date: _____

Indicate the nonconforming condition(s): _____

_____

_____

Corrective measures : _____

_____

_____

Reported by: _____ Date: _____

FORWARD ORIGINAL TO GROUP LEADER RESPONSIBLE FOR CORRECTIVE ACTION
RETAIN COPY IN NC/CA LOG BOOK

SECTION 2 : GROUP LEADER / ASST. GROUP LEADER

Comments or recommendations: _____

_____

_____

Date corrective action completed: _____

Approved by: _____ Date: _____

RETURN ORIGINAL TO NC/CA LOG AND REFERENCE NC/CA # IN RAW DATA
FORWARD COPY TO AE/PM IF RESOLUTION IS PROBLEMATIC

SECTION 3 : QA DEPARTMENT

Corrective action satisfactory? ____Yes ____No

Comments: _____

_____

_____

NC/CA closed by: _____ Date: _____

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Figure 15-3

NC/CA # PE-G-92-

Halliburton NUS Environmental Corporation - Laboratory Services Group
NONCONFORMANCE/CORRECTIVE ACTION RECORD - PE/BQCS FAILURE

SECTION 1 : QA DEPARTMENT

Date/Time: _____

Analyst: _____ Instrument: _____

Department: _____ Bk. & Pg. #: _____

Test: _____ Client: _____

Prep Date: _____ Prep Analyst: _____

Sample Number(s): _____ _____

Reported Value: _____ _____

True Value: _____ _____

Acceptance Range: _____ _____

Reported by: _____ Date: _____

FORWARD ORIGINAL TO GROUP LEADER RESPONSIBLE FOR CORRECTIVE ACTION
RETAIN COPY IN QA NC/CA LOG BOOK

SECTION 2 : GROUP LEADER / ASST. GROUP LEADER Response due: _____

Please investigate the cause(s) of this failure. Report your findings and corrective actions below. Return this form to QA Department.

Findings and root cause: _____

_____

_____

Corrective measures: _____

_____

Reported by: _____ Date: _____

RETURN ORIGINAL TO QA DEPARTMENT

SECTION 3 : QA DEPARTMENT

Corrective action satisfactory? ____Yes ____No

Comments: _____

_____

_____

NC/CA closed by: _____ Date: _____

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This page is intentionally blank.
4/7/24/92

Figure 15-4

AUDIT FINDINGS: SYSTEMS

INTERNAL/QNs

90-098 (CLOSED): No standards, tracers or client samples were received in 1991 that exceeded 10% of the NRC license limit. This quality notice was generated in response to the receipt of the Sirrine samples in 1987.

90-099 (CLOSED): A Radioactive Material Request Form was completed and submitted to the RSO for review and approval for low-level calibration standards and tracers on May 31, 1991.

90-100 (CLOSED): The Po-210 button source has sufficient activity to serve as a GPC performance check for gross alpha/beta analyses. However, the next source shall be Th-230 source that has a sufficiently long half-life.

90-104 (CLOSED): The gamma spec pole-zero optimalizations were performed by the RSO on November 27, 1990 for systems 1 and 2 and January 25, 1991 for system 3. The next annual calibrations and pole-zero settings are awaiting the move to the newly remodeled counting room set for January 1991. The optimalizations are recorded in the maintenance logs, 92-88 p. 80 and 291-90 p. 12.

90-105 (OPEN): The control charting for the various systems performance checks was reviewed. However, some of the systems check charts reviewed lacked necessary information and overlapping limits made them difficult to discern. See the control chart review section of this report.

COMMITTMENT TO CLOSE	DATE: 2/1/92	GL: WK

90-106 (CLOSED): Control charting of gamma spec systems background and performance checks have been performed since the systems went on-line in February 1991. The proper QC checks were worked out with the QAD for K-40 and mixed gamma emitting radionuclide determination analyses.

90-107 (CLOSED): Gamma spec QC checks were arranged with the QAD prior to the start-up of the ENSR/ERM K-40 analyses in February 1991. QC data is submitted to the QAD for evaluation and statistical calculation of control limits. For soil samples, an aqueous method blank and LCS are prepared and counted. For mixed radionuclide work, an EMSL-LV Gamma in Water Cross-Check Study shall be analyzed as an LCS.

91-009 (OPEN): Training records remain incomplete and unrevised.

COMMITTMENT TO CLOSE	DATE: 1/20/92	GL: WK

Figure 15-5

AUDIT FINDINGS FOLLOW UP

HALLIBURTON NUS ENVIRONMENTAL CORPORATION
LAB SERVICES GROUP

AUDIT FINDINGS FOLLOW-UP REPORT

SECTION ONE: Auditor completes for findings not dealt with via a quality notice at the time the audit report is finalized.

Audit: _____
Auditor: _____ Date: _____
Finding: _____
_____
_____
Group Leader: _____ Corrective Action Commitment Date: _____

SECTION TWO: Auditor completes during follow-up activities. Group Leader must acknowledge overdue corrective action by initialing and dating the auditor's notation below and providing a corrective action plan on the back of this form.

DATE	INITIALS	CORRECTIVE ACTION STATUS

SECTION THREE: Auditor completes upon closure.

Auditor: _____ Date: _____
Basis for closure: _____
_____

Figure 15-5 (Continued)

Group Leader completes if corrective action is overdue.			
DATE	INITIALS	CORRECTIVE ACTION	COMPLETION DATE

Figure 15-6

QUALITY NOTICE

HALLIBURTON NUS Environmental Corporation Laboratory Services Group	QN NO:	Activity/Program/Project
	Response Assigned To:	Due Date:

Requirement(s):

See Attachment ☐

Condition Observed/Rationale:

See Attachment ☐

Reported by:	Date:
Management Concurrence:	Date:

Figure 15-6 (Continued)

RESPONSE: Complete Each Item

1. Findings of root cause investigation:

2. Plans for corrective action, immediate and long term to preclude recurrence:

3. Scheduled date(s) for corrective action completion: _____

Response submitted by:	Date:
QUALITY ASSURANCE DEPARTMENTAL REVIEW Corrective Action Disposition: See Attachment: ☐	
Corrective Action Verified and QN Closed by:	Date:

CORRECTIVE ACTION

1.0 PURPOSE AND APPLICABILITY

This procedure describes the mechanisms by which corrective actions for nonconformances detected through routine sampling and laboratory operations, or systems audits are identified and closed. This procedure is applicable to all LSG operations. It interfaces directly with the following LSG Procedures.

- o QA-7, Laboratory Sample Custody
- o QA-8, Laboratory Quality Control
- o QA-10, Data Handling
- o QA-11, Systems Audits
- o QA-12, Performance Audits
- o QA-14, Data Quality Assessment Procedures

2.0 RESPONSIBILITIES

2.1 OPERATIONS MANAGERS, GROUP LEADERS, AND FIELD SUPERVISORS

The Laboratory Operations Managers, Field Operations Manager, Group Leaders, and Field Supervisors determine appropriate measures to correct nonconformances identified during routine laboratory operations and systems audits, and are responsible for implementing these actions and for providing feedback to the Quality Assurance Department on progress of corrective actions.

2.2 QUALITY ASSURANCE DEPARTMENT

The Quality Assurance Department (QAD) performs follow-up activities to ensure that any corrective action is implemented, and effective in resolving the nonconformances.

3.0 PROCEDURE

3.1 CORRECTIVE ACTIONS FOR NONCONFORMANCES IDENTIFIED DURING ROUTINE LABORATORY OPERATIONS

3.1.1 Nonconformances can occur at any time during routine laboratory operations -- during sample bottle preparation, sample receipt, sample analysis, and data reduction and reporting. When a nonconformance is immediately correctable (i.e., fully correctable by the person identifying the nonconformance within the same work shift), corrective action need only be documented through the records routinely generated for that activity. However, when corrective action cannot be completed by the person identifying the nonconformance within the same work shift, a nonconformance/corrective action record (Figure 15-1 for Sample Control, and Figure 15-2 for Sample Analysis) is completed.

3.1.2 The nonconformance/corrective action record is a tool by which problems and their consequences, and corrective action measures and their outcomes are documented and communicated. These records are used as follows:

"Nonconformance/Corrective Action Record -- Sample Control:" The individual reporting the nonconformance completes the first two sections of the form. The AE, Group Leader, or supervisor of the department reviews the corrective action taken, and approves it or indicates additional measures to be taken. Copies of the form are distributed to Group Leaders of the appropriate departments and to the QAD. The original form is filed with the sample log-in sheet.

"Nonconformance/Corrective Action Recorded -- Sample Analysis:" The individual reporting the nonconformance completes the first two sections of the form. The Group Leader or Assistant Group leader reviews the corrective action taken, and approves it or indicates additional measures to be taken. The original form is filed with the raw data. A copy of the form is forwarded to the QAD. A second copy is forwarded to the CSD Manager whenever the nonconformance impacts turnaround commitments and/or is not correctable. When another department is involved in the corrective action, as when a sample must be re-extracted when surrogate recoveries exceed acceptance limits, a copy of the form is forwarded to the Group leader of that department.

3.1.3 The QAD also evaluates the corrective action for appropriateness and completeness, and requests additional corrective measures when warranted. The QAD also determines whether the nature and extent of nonconformance warrants long-term monitoring. If so, this is summarized on the QA copy of the form and pursued.

3.1.3 During monthly quality control meetings, the QAD discusses favorable and unfavorable trends evident from the nonconformances and corrective actions reported.

3.2 CORRECTIVE ACTIONS FOR SYSTEMS AUDIT FINDINGS

Nonconformances identified through systems audits are documented on quality notices (Figure 15-3) in order to track corrective actions. (See LSG Procedure QA-11.) Quality notices are distributed to personnel responsible for corrective action along with the systems audit report (internal audits) or audit summary (external audits). Their disposition is described below.

3.2.1 A log of quality notices is maintained by the QAD in order to track corrective action completion.

3.2.2 Upon receipt of a quality notice, the responsible management staff completes the response section of the quality notice, addressing each of the four topics:

- o Root cause assessment.
- o Corrective action for immediate problem(s).
- o Corrective action to preclude recurrence of the problem.
- o Schedule (dates) for corrective action implementation.

The form and any supporting documentation is returned to QAD. If a response is not received by the due date, the QAD issues one reminder, allowing no more than 5 working days to respond. Failure to respond or to initiate timely corrective action results in referral of the nonconformance to the Assistant General Manager for resolution.

3.2.4 The QAD evaluate quality notice responses. If a response is insufficient or requires clarification, the quality notice is returned further action.

3.2.5 Monthly, at a minimum, the QAD verifies that corrective actions have been implemented in accordance with quality

3.2.5 Monthly, at a minimum, the QAD verifies that corrective actions have been implemented in accordance with quality notice response commitments. Verification is documented on the back of the quality notice form. When corrective actions are satisfactory, the quality notice is closed. Closure is noted on the corrective action log and the quality notice form. A copy of the form acknowledging closure is sent to the respondent; the original form is included with the program monitoring report (internal audit) or the audit summary (external audits).

3.2.6 If closure of the item will require more time than was designated, the QAD may grant an extension. Further extensions may be granted on a case-by-case basis by the Assistant General Manager.

Failure to complete corrective actions within a reasonable time frame results in referral of the nonconformance to the Assistant General Manager for resolution.

4.0 RECORDS

The following records are maintained in support of this procedure in accordance with LSG Procedure QA-20, Quality Assurance Records.

- Nonconformance/corrective action records.
- Corrective action log, quality notices, and supporting documentation.

Figure 15-1

NUS CORPORATION	NONCONFORMANCE/CORRECTIVE ACTION RECORD - SAMPLE CONTROL	LABORATORY SERVICES GROUP

Copies:
- o Check-in
- o Bottle Prep
- o CSD Manager
- o QA Department
- o Metals
- o GC
- o GC/MS
- o Organic Prep
- o Inorganics
- o RCRA/Geo
- o Metals Preparation
- o Bioassay
- o Industrial Hygiene
- o Radiochemistry
- o Other _____
- _____
- _____

Sample Number(s): _____

Client(s): _____

Indicate the nonconforming condition(s):

- o Sample broken
- o Sample missing
- o Sample mislabeled
- o Other: _____
- o Incomplete information received with samples
- o Sample stored improperly
- o Sample disposed of prematurely

_____

_____

Additional Comments: _____

_____

_____

Corrective measures: _____

_____

_____

Reported by: _____ Date: _____

Reviewed by: _____ Date: _____

Comments: _____

_____

_____

Additional Comments:

Figure 15-2

NUS CORPORATION	NONCONFORMANCE/CORRECTIVE ACTION RECORD - SAMPLE ANALYSIS	LABORATORY SERVICES GROUP

Department: _____ Copies: QA Department
CSD Manager
Other: _____

Test: _____ Date/Time: _____

Sample Number(s): _____ Instrument: _____

Client(s): _____

Indicate the nonconforming condition(s):

- o Hold time
- o Tune
- o Initial calibration
- o Continuing calibration
- o Calibration verification
- o Internal standard area/RRT
- o Surrogate spike recovery
- o Retention time shift
- o DDT Breakdown
- o MS and/or MSD recovery
- o Duplicates or MS/MSD precision
- o Lab control sample recovery
- o Method blank contaminants
- o Calibration blank shift
- o Performance evaluation failure
- o Other: _____

Additional comments: _____

Corrective measures: _____

Reported by: _____ Date: _____

Reviewed by: _____ Date: _____

Comments: _____

Additional Comments:

Figure 15-3

NUS CORPORATION	QUALITY NOTICE	LABORATORY SERVICES GROUP

AUDIT SN:	QN NO:	PROGRAM/PROJECT:	
PROCEDURE/DOCUMENT REFERENCE:		ACTIVITY:	
RESPONSE ASSIGNED TO:	DUE DATE:	REPORTED BY:	DATE:

REQUIREMENT:

☐ SEE ATTACHMENT

CONDITION OBSERVED:

☐ SEE ATTACHMENT

USE BACK OF FORM FOR RESPONSE

9/89

Figure 15-3 (continued)

RESPONSE		
COMPLETE EACH ITEM. 1. ROOT CAUSE ASSESSMENT: 2. CORRECTIVE ACTION FOR IMMEDIATE PROBLEM(S): 3. CORRECTIVE ACTION TO PRECLUDE RECURRENCE: 4. SCHEDULE (DATES) FOR CORRECTIVE ACTION COMPLETION:		
RESPONSE SUBMITTED BY:		DATE:
QA EVALUATION AND FOLLOW-UP		
REMARKS:		
C/A VERIFIED ☐ YES ☐ N/A	QA CLOSED BY:	DATE:

Halliburton NUS
CORPORATION

NUS LABORATORY
5350 Campbells Run Road
Pittsburgh, Pennsylvania 15205

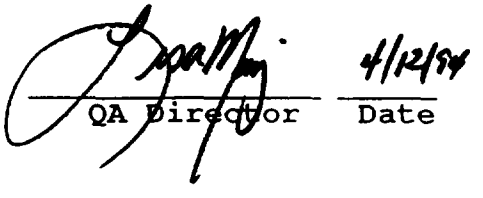
TEL: (412) 747-2500
FAX: (412) 747-2559

STANDARD OPERATING PROCEDURE

PREVENTIVE MAINTENANCE

SECTION ID:	QA-13
REVISION:	0
EFFECTIVE DATE:	04/13/94

APPROVALS:



QA Director — Date

4/12/94

PREVENTIVE MAINTENANCE

1.0 PURPOSE AND APPLICABILITY

This section of the general quality assurance plan describes the NUS Laboratory approach to ensure that instruments used for sample analysis function properly and reliably, and to minimize prolonged instrument downtime so that holding times and sample turnaround commitments can be met.

2.0 RESPONSIBILITIES

2.1 GROUP LEADERS

- Perform assigned preventive maintenance at required intervals. (These tasks may be delegated to analysts within the work group familiar with maintenance and operation of the instruments and equipment.)

- Establish a preventive maintenance schedule for newly acquired equipment, providing any information and assistance necessary to integrate the new equipment into the preventive maintenance reminder scheme.

2.2 INSTRUMENT SPECIALIST

- Perform or supervise in-house preventive maintenance, troubleshooting, and corrective maintenance of major equipment.

- Perform or schedule calibration of test equipment and balances.

2.3 QUALITY ASSURANCE DEPARTMENT (QAD)

- Review maintenance logs annually, at a minimum.

- Distribute reminders for required preventive maintenance performed monthly or less frequently.

3.0 PROCEDURE

3.1 INSTRUMENT MAINTENANCE LOGS

3.1.1 The maintenance history of all major laboratory equipment is documented in instrument maintenance logs as follows.

- In-house preventive maintenance, trouble-shooting, and corrective maintenance are documented in the log by the NUS Laboratory staff member performing the maintenance.

- Maintenance performed by an outside vendor is documented in the maintenance log. An entry is made in the log by the NUS Laboratory staff member signing the service report and the report is stapled to the log book page.

- All maintenance log entries must include a discussion of the problem, the actions taken, and the results of the action. See also NUS Laboratory Procedure AP-021, Preventive Maintenance Documentation. Additionally, following major repairs, instrument output demonstrating performance should retained in the maintenance log to assist in future trouble shooting efforts.

3.1.2 The QAD reviews instrument logs annually, at a minimum. Balance logs are reviewed quarterly.

3.2 TEST EQUIPMENT CALIBRATION

3.2.1 The equipment used to calibrate analytical equipment is NIST certified and/or calibrated periodically against standards having known and valid traceability to recognized standards. Requirements are specified below. See also NUS Laboratory Procedure AP-16, Procurement of Calibration Services by Outside Vendors, for external calibration requirements.

- mV standards and 5-1/2-digit voltmeters are calibrated by an outside vendor annually, at a minimum.

- Glass/mercury thermometers are calibrated against an NIST-certified thermometer annually, at a minimum. A tag identifying the

calibration date and correction factor is physically applied to each thermometer.

- Thermocouples are calibrated against a mV standard and an ice bath annually, at a minimum.

- Class S weights are used to verify weights maintained at the balances. They are calibrated annually against weights whose calibration is traceable to the NIST.

- Weights maintained at the balances are calibrated against Class S weights annually, at a minimum.

- Meters used to measure air uptake of exhaust and fume hood are calibrated annually, at a minimum, by an outside vendor.

3.2.2 Calibration of test equipment is documented in the same fashion as analytical equipment calibrations as described in 3.1.1.

3.3 PREVENTIVE MAINTENANCE OF ANALYTICAL EQUIPMENT

3.3.1 Preventive maintenance (PM) encompasses a variety of operations performed at prescribed intervals:

- specification checks
- calibration
- cleaning
- lubrication
- reconditioning
- adjustments

The purpose of preventive maintenance is two-fold:

- To minimize the occurrence and severity of catastrophic performance losses that result in prolonged equipment downtime.

- To detect and correct more subtle, noncatastrophic performance losses before they have a significant impact on data generation and/or quality.

3.3.2 Preventive maintenance (PM) requirements for analytical equipment are tabulated in Section 3.9. The time frames specified for preventive maintenance activities are minimum requirements; preventive maintenance may be performed more frequently.

The QAD issues reminders (Figure 13-1 or equivalent) for PM due monthly or less frequently. The reminders are issued to the group leader or the instrument specialist, as appropriate, approximately six weeks before the PM due date. This will allow sufficient time to schedule the maintenance so that it can be performed prior to the due date with minimal disruption to sample analysis in most circumstances.

The group leader/instrument specialist is responsible for completion of the PM on or before the due date. Performance of the PM may be delegated, but responsibility for its completion rests with the group leader/instrument specialist. Every effort should be made to keep the preventive maintenance program and supporting documentation current and complete, since failure to do so could result in equipment performance loss.

Calibrations must be completed by the specified due date. If not, the instrument will be tagged "out-of-service" for the analytes of interest pending successful completion of the calibration. If scheduled preventive maintenance -- other than calibration -- cannot be performed on or before the due date, the group leader/instrument specialist must contact the QAD and reach a mutually agreed upon time frame for its completion.

3.3.3 The person performing the preventive maintenance is responsible for documenting the activity in the maintenance log. See NUS Laboratory Procedure AP-021, Preventive Maintenance Documentation, for further instruction on maintenance log entries.

When periodic maintenance involves calibration or calibration verification, a calibration label (Figure 13-2 or equivalent) is applied to the equipment by the person completing the calibration/verification.

3.3.4 Equipment that is out of calibration or requires repair is tagged "out-of-service" (see Figure 13-3 and NUS Laboratory Procedure AP-021, Preventive Maintenance Documentation).

3.3.5 Any change in status, from active to inactive or inactive to active, should be recorded in the maintenance log and discussed by the group leader at the monthly quality assurance meeting.

3.4 REQUESTING IN-HOUSE SERVICE

3.4.1 While preventive maintenance reduces the number and severity of equipment malfunctions, it will not eliminate all malfunctions. Whenever the expertise of the instrument specialist is required to trouble-shoot or repair equipment, the group leader completes a service request form (Figure 13-4).

The form serves three purposes:

- It informs the instrument specialist of problems in writing
- It helps the instrument specialist prioritize work
- It provides a history of the problems encountered by individual instruments and classes of instruments.

This form is also used to schedule in-house maintenance for the facility; it is forwarded to facility maintenance personnel rather than the instrument specialist.

3.4.2 The requester completes Part I of the form and notes the request for service in the instrument maintenance log. The requester should describe the problem on the form as completely as possible. This allows the instrument specialist to evaluate and correct the problem in the most efficient manner. Priority codes are as follows:

- Priority 1 - Immediate repair required. Downtime will have a major impact on overall laboratory performance. Repair to be completed as soon as possible (i.e., within 1 working day or less if parts/service are available).
- Priority 2 - Service to be performed within 5 working days. Limited impact on overall laboratory operations, but significant impact on 1 or more groups. Extended downtime may cause

significant problems.

- Priority 3 - Service to be performed on a scheduled basis. Order of service performed is based on order in which requests are received. Generally service will be performed within 10 to 30 working days. Priority 3 is appropriate when an operable backup system is available.

- Priority 4 - Service to be performed on inactive equipment or low priority maintenance. Service should be performed within 90 days, even if an outside vendor must be used.

3.4.3 Following servicing, the instrument specialist completes Part II of the form. He/she staples the original form into the maintenance log and a copy is forwarded to the requester.

3.5 REQUESTING OUTSIDE MAINTENANCE SERVICES

Whenever the expertise of an outside service specialist is required to trouble-shoot or repair equipment, the group leader confirms the appropriateness of using outside services with the technical operations manager. The request group leader contacts the vendor and schedules the service, then enters the purchase request in the "order" function of the LIMS.

In the event of an emergency, the group leader or instrument specialist may arrange for outside service directly.

3.6 MAJOR EQUIPMENT LIST

3.6.1 All major laboratory equipment is catalogued on a major equipment list. The list identifies equipment by type, make, model, serial number, year of purchase and condition at purchase. The list is updated by the procurement representative/proposal coordinator as equipment is put into or taken out of service.

3.6.2 Equipment that contains radioactive isotopes is listed on the primary equipment list and on an auxiliary radioactive instrument/article inventory. The radioactive instrument/article inventory identifies the type of equipment, its make, model, and serial number, the nuclide and its activity, and the

group leader responsible for the equipment. Group leaders are responsible for timely update of the inventory.

3.6.3 Equipment cannot be moved, modified, or discarded without approval of the technical operations manager.

3.7 NEW EQUIPMENT

Newly acquired equipment must be integrated into the QA program prior to its use in sample analysis.

3.7.1 When new equipment has been ordered, the group leader addresses the following for the instrument in a memorandum to the technical operations manager and the QA director:

- Laboratory facility preparations for installation.
- Who is performing installation (manufacturer, instrument specialist, group leader)
- Performance criteria to be met upon installation.
- Start-up studies to be performed.
- Who is to prepare the SOP and when it will be completed.

3.7.2 During installation and start-up, preliminary demonstrations of equipment performance, such as first chromatograms or raw data, must be retained in the maintenance log. The data will be valuable for later diagnostics.

When installation and start-up are completed, the group leader completes a laboratory equipment status record (Figure 13-5) and forwards it along with the following to the QAD.

- Preventive maintenance program.
- Critical spare parts list.
- Summary of start-up study results.

A laboratory method or operating procedure must outline the following (see also section QA-9 of this plan, Plans and Procedures):

- Step-by-step operation.
- Calibration.
- Quality control program.
- Data collection and reduction.

3.7.3 Instrument manuals supplied by the manufacturer are maintained in the laboratory for reference.

3.8 CRITICAL SPARE PARTS

Each laboratory must retain spare parts deemed to be critical to instrument operation, or must have the ability to obtain critical parts on an overnight basis. A suggested spare parts list follows.

3.8.1 ANALYZERS

3.8.1.1 ALPKEM Autoanalyzers

1) flow cells
2) teflon tubing
3) glass tubing coils
4) distillation heads
5) lamps
6) fuses
7) pens, chart paper and ribbon

3.8.1.2 Total Organic Carbon Analyzers

1) tubing and connectors
2) septa
3) quartz and pyrex wool
4) NDIR screens
5) syringes
6) o-rings
7) UV reactor housing
8) UV reactor cap

9) tubing without connectors
10) UV reactor vessel

3.8.1.3 Total Organic Halogen Analyzers

1) generator working electrode/black
2) generator auxiliary electrode/red
3) reference electrode/white
4) sensor electrode/green
5) pyrolysis tube
6) pushrod assembly
7) cored septa, uncored septa
8) exit tube and inlet tube o-rings
9) heater tape assembly
10) inlet and exit tubes
11) cerefelt
12) quartz boats
13) grey septa
14) GAC-Carbon Plus
15) Titration cell T-620

3.8.2 ATOMIC ABSORPTION/EMISSION INSTRUMENTS

3.8.2.1 Cold Vapor Atomic Absorption Spectrometers

1) absorption cell with windows and gaskets
2) window and gasket replacement kit
3) mercury lamp
4) aeration and connecting (silastic) tubing
5) scrubber kit
6) pump
7) diaphragm replacement kit (includes gasket and 2 valves)
8) photo detector tube
9) tubing clamps
10) out/in fittings

3.8.2.2 Flame Atomic Absorption Spectrometers

1) complete nebulizer assembly

2) impact beads
3) flow spoiler
4) cable and pin assembly
5) o-rings
6) sample injector tubing
7) nitrons oxide burner
8) EDL and deturium lamps
9) red filter
10) fuses
11) photomultiplier tube
12) burner head, acetylene, 4-inch

3.8.2.3 Graphite Furnace Atomic Absorption Spectrometers

1) contact cylinders
2) windows
3) injector tips
4) o-rings
5) graphite tubes
6) platforms
7) gaskets
8) EDL and deturium lamps
9) capillary tubing for autosamplers
10) adapters for hollow cathode lamps
11) platform alignment tool
12) outlet valves

3.8.2.4 Inductively Coupled Plasma Spectrometers

1) argon tubing (internal)
2) torch assembly
3) RF coil
4) o-rings
5) nebulizer
6) sample injector
7) bonnets
8) carbon tips
9) spray chamber
10) high solids nebulizer
12) fuses
13) capillary tubing for autosamplers

3.8.3 Liquid Chromatographs

1) gaskets
2) o-rings
3) pump rebuilding parts (seals, stop valves, etc.)
4) spare pumps
5) tubing
6) appropriate Swage lock fittings

3.8.4 Gas Chromatographs

1) photo ionization detector (spare component)
2) electron capture detector (spare component)
3) analytical columns
4) septa
5) syringes
6) ferrules
7) solvent pump for electrolytic conductivity detectors

3.8.5 Gas Chromatograph/Mass Spectrometers

1) back-up mechanical vacuum pump
2) copper gaskets
3) glass jet separators for VOAs
4) capillary columns
5) septa, syringes and ferrurels
6) 1/16 to 1/4 inch fittings (Swagelock)
7) appropriate o-rings
8) turbo molecular pumps
9) magnetic tapes
10) voltometer; electronic trouble-shooting tools
11) Tekmar purge and trap component, heated transfer line and multipart valve
12) electron multilpiers
13) pump oil
14) turbo pump oil
15) diffusion pump oil
16) filaments
17) source parts

3.8.6 CALORIMETER/OXYGEN BOMB

3.8.6.1 Calorimeter

1) thermometer 19-35°C
2) thermometer bracket
3) thermometer reading lens
4) stirrer drive belt
5) colorimeter jacket with cover
6) oxygen combustion bomb

3.8.6.2 Oxygen Bomb

1) o-rings (assorted)
2) bare bomb head
3) check valve
4) deflector nut
5) loop electrode with sleeve
6) straight electrode with sleeve
7) electrode core
8) valve knob
9) lock nut
10) valve needle
11) outlet valve body
12) Kel-F valve seat
13) oxygen filling connection
14) toggle relief valve
15) flexible tube assembly
16) knurled union nut
17) union fitting
18) o-rings
19) slip connector

3.8.7 CONDUCTIVITY CELLS

1) spare cells
2) temperature probe

3.8.8 DEIONIZED WATER SYSTEM

1) carton of solids filters
2) spare cells (i.e., electrodes which monitors resistivity)
3) recycle pump

3.8.9 DISSOLVED OXYGEN PROBES

1) spare probes
2) membranes

3.8.10 ELECTRODES

Spare ammonia sensing, pH and fluoride electrodes

3.8.11 METERS

Spare meter units

3.8.12 RADIOCHEMISTRY COUNTERS

3.8.12.1 Gamma Spectrometers

1) TC 950 power supply (2)
2) TC 244 amp (2)

3.8.12.2 Gas Proportional Counters

1) TC 952 high voltage supply
2) mylar windows

3.8.12.3 Alpha Spectrometers

1) silicon surface barrier detector
2) PD-500-100-25-cm (2)
3) TC 265 amp
4) TC 265 alpha spectrometers (7)

3.8.13 SPECTROPHOTOMETERS

1) 1 cm and 5 cm cells

2) bulbs
3) fuses

3.8.14 TITRIMETERS

3.8.14 Karl Fisher

1) reaction vessel gasket
2) sample septum
3) flanged teflon delivery tip
4) thumb screws
5) septa
6) electrode and septum port nuts
7) o-rings for electrode and septum
8) vent port nut o-ring
9) vessel seal gasket
10) septum port plug
11) connector tubing assembly o-ring

3.9 PREVENTIVE MAINTENANCE SCHEDULES

Preventive maintenance schedules for the following equipment are listed on tables at the end of this procedure.

Analyzers

ALPKEM Autoanalyzer
Total Organic Carbon Analyzer, Dohrman DC-80
Total Organic Halogen Analyzers

Atomic Absorption/Emission Instruments

Cold Vapor AA Units (Mercury Analyzer)
Flame AA Spectrophotometer
Graphite Furnace AA Spectrophotometer
Inductively Coupled Plasma Spectrometer

Autoclaves

Balances

Chromatographs

Gas Chromatograph
Gas Chromatograph/Mass Spectrometer
Liquid Chromatograph

Calorimeters

Centrifuges

Conductivity Cells

Deionized (DI) Water System

Dissolved Oxygen Probes

Electrodes

General Care
General Calibration Checks
Trouble-Shooting
Ammonia Gas-Sensing Electrode
Fluoride Electrode
pH Electrode

Extractors, Toxicity

Bottle Extractor
Zero Headspace Extractor

Heating Units

Incubator
Muffle Furnace
Oven

Hoods

Exhaust Hood
Fume Hood

Meters, pH/mV

Personnel Computers

Purge and Trap Units

Radiochemistry Counters

Alpha Spectrometer
Gamma Spectrometer
Gas Proportional Counter
Liquid Scintillation Counter
Scintillation Cell Counter
Survey Meter

Refrigeration Units

Cooler
Freezer

Recorders

Sonicators

Spectrophotometers

Infrared Spectrophotometer
Turbidimeter
UV-Visible Spectrometer

Titrimeters

Karl Fisher

Water Baths

4.0 RECORDS

The following records are maintained in support of this procedure in accordance with section QA-20 of this plan, Quality Assurance Records.

- Instrument maintenance logs
- Preventive maintenance reminders
- Laboratory equipment status records
- Service request forms
- Major equipment list
- Radioactive instrument/article inventory
- Instruction manuals supplied by equipment manufacturers
- Preliminary studies and demonstrations of equipment performance following installation and major repair

FIGURE 13-1

PREVENTIVE MAINTENANCE REMINDER

ISSUED TO: _____ DATE: _____

SERVICE REQUIRED

INSTRUMENT: _____
(Make/Model/Serial No.)

PM TO BE PERFORMED: _____

DUE DATE: _____

SERVICE COMPLETED

BY: _____

DATE: _____

DOCUMENTED: _____
(Maintenance Log Book and Page Number)

FIGURE 13-2

CALIBRATION LABEL

NUS LABORATORY

EQUIPMENT: _____

CALIBRATED DATE: _____

VERIFIED DATE: _____

DUE DATE: _____

(This page left intentionally blank.)

FIGURE 13-3

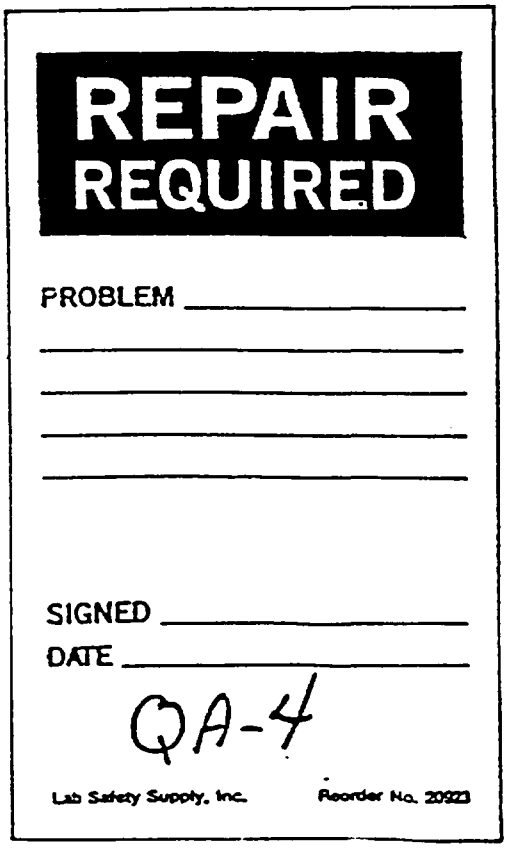

REPAIR
REQUIRED
PROBLEM
SIGNED
DATE
QA-4
Lab Safety Supply, Inc.
Reorder No. 20923

FIGURE 13-4

SERVICE REQUEST FORM

PART I - SERVICE REQUIRED

INSTRUMENT OR FACILITY SYSTEM: MAKE MODEL SERIAL NO.

DESCRIPTION OF PROBLEM (Include date and time first occurred):

PRIORITY CODE (1.4) (See back of form):

REQUESTER: _____ DATE: _____

PART II - SERVICE PERFORMED

FAULT CONDITION DIAGNOSIS:

CORRECTIVE ACTION:

SERVICED BY: _____ DATE: _____

DISTRIBUTION: Equipment file (original)
Requester

FIGURE 13-5

LABORATORY EQUIPMENT STATUS RECORD

Halliburton NUS CORPORATION
5350 Campbells Run Road
Pittsburgh, PA 15205

LABORATORY EQUIPMENT
STATUS RECORD

TYPE	PURCHASE DATE MONTH YEAR
MANUFACTURER	
MODEL	GROUP LEADER
SERIAL NO.	DATE
LOCATION	
Placed into service as of:	

For new equipment, review service manuals and list all preventive maintenance and its frequency (Weekly, Annually, etc.) required for this instrument:

PLEASE FORWARD TO QA DEPARTMENT

QAPM Name _____ File Created _____

LIMS Instrument Code _____ File Closed _____

ANALYZERS

Equipment	Frequency	Preventative Maintenance Requirements
Autoanalyzer, Alpkem 305A	Daily (Analyst)	Evaluate the sensitivity and reproducibility of each parameter run during standardization. When one or both characteristics degrade, trouble-shoot the system.
		Clean platen surfaces of the 302 pump and empty waste containers.
	Quarterly (Analyst)	Wipe pump rollers of the 302 pump with isopropyl alcohol and clean manifolds by pumping Kem Wash (TM) through the analytical cartridge.
		Replace pump tubing in the analytical cartridge.
	Quarterly (Analyst)	Remove pump bodies and clean roller cage. Clean the fan and lubricate the gears of the 302 pump.
	Monthly (Analyst)	Clean the wash reservoir.
	Semi-annually (Analyst)	Replace drain tubing in the cartridge module and replace the transmission tubing in the analytical cartridge.
Total Organic Carbon Analyzer, Dohrman DC-80	Daily (Analyst)	Evaluate the sensitivity and reproducibility of the system during standardization as follows. With the calibration off, check the reading of a 400 mg/L and a 10 mg/L standard. They should read 300 ± 75 and 7.5 ± 1.85 respectively. A duplicate injection of the standards should be within 2% of the first injection. If this criteria is not met, trouble-shoot the system.
		Inspect injection port septum.

Equipment	Frequency	Preventative Maintenance Requirements
		Inspect the tin scrubber. Change the tin if discolored.
		Inspect the pump tubing and pump flow. (Flow should be 2 mL/min.)
		Clean up leaks or spills on the interior or exterior of the reaction module.
	Weekly (Analyst)	Check purge gas flow and the in-line filter.
	Annually (Analyst)	Run a linearity check for the entire working range. Repeat the check following cleaning of the IR detector or when quality control checks indicate that the current curve may not be valid.
Total Organic Halogen Analyzer, Dohrman	Daily (Analyst)	Check the following: • exit tube and quartz wool • titration cell for lodged bubbles • inlet area for carbon spills • electrolyte level
		Obtain a steady baseline.
		Clean the quartz boat.
		Evaluate the sensitivity and reproducibility of the system during standardization utilizing a 100 mg/L standard. When one or both characteristics degrade, trouble-shoot the system.
	Monthly (Analyst)	Clean the stainless steel sample inlet tube, and POX sparger if system is so equipped.
	Semi-annually (Instrument Specialist)	Calibrate the microcoulometer/integrator using internal circuits, and calibrate the pyrolysis tube and sparger oven temperatures.

Equipment	Frequency	Preventative Maintenance Requirements
	Annually (Analyst)	Run a linearity check covering the entire working range. Repeat the check following major reapir or whenever control checks indicate that the direct readout may not be valid.
Total Organic Halogen Analyzer, 10 Sigma	Daily (Analyst)	Clean the silver sensor with Commet™, or equivalent.
		Change the outer reference solution (1 M KNO_3).
		Change the counter electrode solution (10% KNO_3).
		Clean outer counter electrode wire with Commet™, or equivalent.
		Rinse cell body with reagent water before and after use.
		Discard electrolyte solution and fill cell body with reagent water.
		Replace dehydration tube solution (conc. H^2SO^4)
	Minthly (Analyst)	Change inner reference solution.

ATOMIC ABSORPTION/EMISSION INSTRUMENTS

Equipment	Frequency	Preventative Maintenance Requirements
Mercury Analyzer	Daily (Analyst)	Calculate the characteristic mass measurement after running an appropriate standard. If there is over a 20% change in the mass measurement or reproducibility degrades, trouble-shoot the system.
		Change drying tube.
	Semi-annual or as required (Instrument Specialist)	Clean or if necessary replace the sample tube and windows; replace o-rings.
		Clean pump by flushing with deionized water, replace pump if background noise becom very high.
		Replace activated carbon trap.
		Inspect and replace tubing as required.
	Annually (Instrument Specialist)	Clean printed circuit boards and switches, replace any that are worn or damaged.
		Check power supply voltages.
Flame AA	Daily (Analyst)	Calculate the characteristic mass measurement after running an appropriate standard. If there is over a 20% change in the mass measurement or reproducibility degrades, trouble-shoot the system.
		Clean the slot and face of burner head of flame units carefully. If there is a heavy build-up of solids, clean burner heads by sonication in a weak acid solution (1-3% v/v nitric acid) for 15 to 30 minutes followed by a deionized water rinse. Dry with acetone.

Equipment	Frequency	Preventative Maintenance Requirements
		Flush the burner chamber with DI water following analysis of samples high in dissolved solids at end of day.
	Annually (Instrument Specialist)	Clean spectrometer optics. Visually inspect printed circuit boards throughout the system, clean and repair as necessary.
Graphite Furnace AA	Daily (Analyst)	Inspect graphite tube and contact cylinders of furnace units for wear and deposits; clean according to manufacturer's recommendations or replace as necessary. Clean windows according to instrument manufacturer's recommendations.
		Calculate the characteristic mass Graphite Furnace AA measurement for furnace units and the characteristic concentration measurement for flame units utilizing the appropriate standard for each element to be analyzed on that day. If there is over a 20% change from the constant value, in either measurement or if reproducibility degrades, trouble-shoot the system (e.g., check system set up, prepare fresh standards, inspect and clean nebulizer if necessary, check auto sampler capillary, replace hollow cathode, electrodless discharge and/or deuterium arc lamps).
	Annually (Instrument Specialist)	Clean spectrometer optics. Visually inspect printed circuit boards throughout the system, clean and repair as necessary. Drain and replace chiller pump oil. Clean filters on furnaces. Calibrate EDL power supplies.

Equipment	Frequency	Preventative Maintenance Requirements
Inductively Coupled Plasma	Daily (Analyst)	Evaluate yittrium sensitivity and reproducibility during standardization. When one or both characteristics degrade, trouble-shoot the system (e.g., check system set-up, prepare fresh working standards from stock solution, inspect the sample introduction assembly-torch, injector tube, spray chamber, nebulizer, pump tubing and sample tip for wear or deposits, clean and replace components as necessary).
		Release the clamp on the peristallic pump tubing at the end of the day.
		Inspect autosampler and tubing for solids buildup, cracking or wear. Clean or repl components as required.
	Weekly (Analyst)	**Remove torch and replace with clean spare, clean used torch and inspect it for wear, put it aside for next scheduled cleaning. Check torch alignment by running appropriate internal checks. A sensitivity check should be performed after replacement of the torch.** **Inspect the spectrometer lens. Clean lens with a Q-tip and alcohol as necessary.**
		Check pump delivery rate. If it differs from the set flow by more than 10%, replace the tubing. Inspect the coil. Clean or replace if signs of surface oxidatoin are apparent. Replace oil in vacuum pump.
	Biweekly (Analyst)	Change peristallic pump tubing, if neces adjust pump pressure to deliver a consta and even sample flow.

Equipment	Frequency	Preventative Maintenance Requirements
	Monthly (Analyst)	Check oil level in the vacuum pump. Refill as necessary. Remove dust from the intake air filters.
	Semi-annually (Analyst)	Clean and oil roller assembly of peristallic pump.

AUTOCLAVES

Equipment	Frequency	Preventative Maintenance Requirements
Autoclave	Semi-annually (Analyst)	Verify the accuracy of the temperature gauge using a maximum temperature reading thermometer.

BALANCES

Equipment	Frequency	Preventative Maintenance Requirements
Balances	Daily (Analyst)	Verify balance calibration. Each check weight should read within its true weight ±2 in the right-most digit read by the balance during the initial weighing and ±3 in subsequent weighings.
		Carefully clean the balance pan, the balance, and the area around the balance after each use.
	Annually (Outside Vendor)	Clean and calibrate balances.

CHROMATOGRAPHS

Equipment	Frequency	Preventative Maintenance Requirements
Gas Chromatographs	Daily (Analyst)	Inject an appropriate solvent to evaluate the flatness of the baseline, retention time, peak area and peak shape. If any anomalies are found, trouble-shoot the system by first cleaning the injector, then, if necessary, changing the columns, and then checking the detectors electronic system.
		Evaluate the sensitivity and reproducibility of the analytical system during standardization. When one or both characteristics degrade, trouble-shoot the system.
	Quarterly (Analyst)	Clean and change all air filters, as applicable to the type of instrument.
	Semi-Annually (Analyst)	Perform a wipe test on each electron of radioactive material.
	Annually (Instrument Specialist)	Clean the printed circuit boards and inspect them for broken traces, evidence of overheating, etc.
		Verify injector, detector and column oven tempera-tures. Verify and record oven temperature program rates.
		Carefully vacuum the inside rear of the instruments to remove dust.
Gas Chromatograph/Mass Spectrometers	Daily (Analyst)	Run Decafluorotriphenyl Phosphine (DFTPP) or Bromofluorobenzene (BFB) to verify mass spectrometer sensitivity and tuning.
		Evaluate the sensitivity and reproducibility of the system during standardization. When one or both characteristics degrade, trouble-shoot the system.

Equipment	Frequency	Preventative Maintenance Requirements
	Quarterly (Analyst)	Clean and change all air filters.
		Change the mechanical pump oil.
		Clean and change if necessary the fan screens.
	Following Source or Rod Cleaning (Analyst)	Run Perfluorotributylamine (FC-43) to verify resolution and mass range calibration after cleaning the source or rods.
	Semi-Annually (Instrument Specialist)	Check turbo pump oil levels on INCOS 50 Models.
	Annually (Instrument Specialist)	Inspect and clean the power supply and printed circuit boards.
		Clean and replace if necessary, the water filters on FINN 4500 models.
	Tri-Annually (Analyst)	Change the diffusion pump oil.
Liquid Chromatographs	Daily (Analyst)	Evaluate the sensitivity and reproducibility of the system during standardization. When one or both characteristics degrade, trouble-shoot the system.
		Flush instrument with a cleaning solvent after each use.
	Semi-Annually (Instrument Specialist)	Check the solvent delivery system and flow rate, using the same type of column and instrument conditions each time.
		Replace the reservoir filter and pump inlet filter.
		Check the inlet and outlet check valve.

Equipment	Frequency	Preventative Maintenance Requirements
		Check the quartz cell for deposits, clean as necessary according to manufacturer's instructions.
		Lubricate the pump gear. (Not required for units equipped with self-lubricating pumps.)
	Annually (Instrument Specialist)	For instruments so equipped, inspect the optical filter and lamp. Clean or replace as necessary.
		Replace plunger seals and the TFE plug seal in the injector.

CALORIMETERS

Equipment	Frequency	Preventative Maintenance Requirements
Calorimeters	Daily (Analyst)	Run a benzoic acid standard.
		Clean the jacket, head, cup, and wires after each firing, using soap and water followed by tap and deionized water rinses.
	As required (Analyst)	Replace the firing wire.

CENTRIFUGES

Equipment	Frequency	Preventative Maintenance Requirements
Centrifuges	Annually (Instrument Specialist)	Clean and inspect the motor. Repair as necessary.

CONDUCTIVITY CELLS

Equipment	Frequency	Preventative Maintenance Requirements
Conductivity Cells, YSI 3400	Daily (Analyst)	Inspect the cell. If platinum black coating appears to be thin or flaking off, clean the electrodes and replatinize as described in the instruction manual.
		Store the cell in deionized water when not in use.
	Quarterly (Analyst)	Run a series of 4 standards ranging from 200 to 10,000 umhos to determine the linearity of the calibration curve. Calculate calibration factor.
		Clean the gold and silver leads.

DI WATER SYSTEM

Equipment	Frequency	Preventative Maintenance Requirements
DI Water System	Daily (Surveillance Monitor)	Record the resistivity reading on the secondary meter which monitors the water recycling through the closed loop to the laboratories and back. The meter should read 12 or greater megaohms. The reading should be recorded in the surveillance log. Any major drop in value should be reported to the instrument specialist.
	Daily (Inorganic Laboratory Analyst)	Record the conductivity of the finished water to insure that the conductivity is <2 umhos/cm.
	Monthly (Facility Technician)	Change the solids filter monthly at a minimum, or whenever a restriction in make-up service water is observed, whichever is more frequent.
	Monthly (IO Lab Analyst)	Measure DI water system water quality at point of use throughout the facility. See NUS Laboratory Procedure AP-002, Reagent Water and Controlled Temperature Unit Quality Control Surveillance, for specific instructions.
	As needed (Instrument Specialist)	Replace recycle pumps as they become noisy or worn.
	Quarterly (Outside Vendor)	The polishing filters should be replaced quarterly, sooner if there were drought or low flow conditions for any length of time.
	Annually (Instrument Specialist)	Clean the cells (i.e., in the electrode which measures resistivity) in the meter, replace if faulty.
		Calibrate the in-line conductivity meter.

DISSOLVED OXYGEN PROBES

Equipment	Frequency	Preventative Maintenance Requirements
Dissolved Oxygen Probes	Daily (Analyst)	Check the membrane for deterioration. Replace membrane and refill the KCL solution as needed.
		Check for tarnish/deterioration on the gold cathode and silver anode; clean if necessary.
		Store probe in BOD bottle one half full of deionized (DI) water. Calibrate against water saturated air in storage bottle. (Allow the probe to warm up before use.) Replace DI water in bottle when contaminated, and rinse the end of probe with DI water before storage.

ELECTRODES, GENERAL

Equipment	Frequency	Preventative Maintenance Requirements
All Electrodes	Daily (Analyst)	General Care: Handle gently at all times. Check filling solutions and storage solutions daily. Ensure that all electrodes are properly capped and immersed in storage solution.
		General Calibration Checks: Normal slope for all electrodes is approximately 58 mV ± 3 mV; if outside range, check electrode. Check calibration every two (2) hours, whenever ambient/solution temperature changes by 2°C or more, or after every 20 analyses, whichever is more frequent.
	As needed (Analyst)	Trouble-shooting: Off-Scale/Over Range Reading -- Check the following: • connection to meter • filling solution • inner body/sensor junction • meter diagnostics • standard/sample matrix

Equipment	Frequency	Preventative Maintenance Requirements
		Erratic (Noisy) Reading -- Check the following: • membrane/sensor body junction cone • inner body • meter
		Drifting Reading -- Check the following: • filling solution (both amount and type) • matrix • membrane/sensor body/junction cone • solution temperature • inner body
All Electrodes	As needed (Analyst) (Continued)	Low or No Slope Prepare fresh standards from stock solution; perform checks listed for drift.

ELECTRODES, SPECIFIC INSTRUMENTS

Equipment	Frequency	Preventative Maintenance Requirements
Ammonia-Gas Sensing Electrodes	Daily (Analyst)	Check membrane closely for any deterioration, discoloration or wetting. Change membrane and filling solution if necessary. (Allow 2 hours stabilization time thereafter.)
		always keep membrane immersed - either in sample or standard during readings, or in 10 mg/L NH_3-N with 10 M NaOH added between readings. (Use pH 4 buffer with added NaCL between low level ammonia readings. Never store in pH 4 buffer, however.)
		Store up to one week in 1000 mg/L NH_3 without NaOH. Replace storage solution as needed.
	Quarterly (Analyst)	Perform inner body check and replace filling solution.
Fluoride Electrodes Refillable Fluoride Electrodes	Daily (Analyst)	Inspect junction cone and o-ring for clogging or crystallization. If present disassemble, rinse with deionized water and filling solution, reassemble, and add filling solution. Allow at least 2 hours to stabilize.
		Check the filling solution level. Add filling solution to level 1 inch above sample in beakers at least one hour before use.
		Store in 19 mg/L fluoride standard dilution.
Nonrefillable Fluoride Electrodes	Daily (Analyst)	Store covered with cap in place.
		Stabilize 1/2 hour prior to use.

Equipment	Frequency	Preventative Maintenance Requirements
Reference Electrodes	Daily (Analyst)	Inspect junction cone and o-ring for clogging and crystallization. If present, disassemble, rinse with DI water and filling solution, reassemble, and add solution. Allow at least two (2) hours to stabilize.
		Check the filling solution level. Add filling solution to level 1 inch above sample in beakers at least one hour before use.
		Store in tap water.
pH Electrodes	Daily (Analyst)	Check glass sensor bear and guard for damage.
		Ensure that no air bubbles are present in the filling gel; if present, shake electrode downward to remove.
pH Electrodes (Continued)	Daily (Analyst) (Continued)	Clean with one or more of the following: • DI water (and cotton swab if needed) • Methanol or isopropanol (Never use any other solvent). • 0.1 M HCL or HNO_3 • 0.1 M Tetrasodium EDTA solution **IMPORTANT:** When using any cleaning agent other than DI water, restore the electrode function by soaking at least 30 minutes in pH 7 buffer before use or storage.
		Store the electrode with protective cap over sensor. ensure that cap is moistened with DI water.

TOXICITY EXTRACTORS

Equipment	Frequency	Preventative Maintenance Requirements
Bottle Extractors	Quarterly (Analyst)	Oil the extractor motor.
		Check the number of revolutions per minute. Adjust if necessary.
Zero Headspace Extractors	Daily (Analyst)	Inspect seals and screens; replace as necessary.

HEATING UNITS

Equipment	Frequency	Preventative Maintenance Requirements
Incubators	Daily (Analyst)	Record incubator temperature daily.
Muffle Furnaces	Semi-Annually (Instrument Specialist)	Check the accuracy of the temperature gauge.
		Perform a thermocouple check.
Ovens	Each Use (Analyst)	Record oven temperature each time samples or reagents are put into or removed from the oven. Verify that oven temperature is within required range. If it is not, make an appropriate adjustment.

HOODS

Equipment	Frequency	Preventative Maintenance Requirements
Exhaust Hoods	Biennially (Facility Maintenance Technician)	Check drive belts for fans, replace as necessary.
		Lubricate the fans.
	Annually (Chemical Hygiene Officer)	Measure the air uptake with the air velocity meter to verify that the air uptake is the same value as that measured when the hood was first installed (i.e., brand new). Record the value in the maintenance log as cubic feet per minute.
Fume Hoods	Quarterly (Chemical Hygiene Officer)	Perform a full face velocity traverse after biennial inspection and repairs, and quarterly thereafter.
	Biennially (Analyst)	Prior to the maintenance inspection, clean the interior of the hood thoroughly.
	Biennially (Facility Maintenance Technician)	Lubricate the fans.
		Inspect fan drive belt, replace as necessary.

METERS, mV/pH

Equipment	Frequency	Preventative Maintenance Requirements
mV/pH Meters	Semi-Annually (Instrument Specialist)	Calibrate the member against a millivolt standard.
	Annually (Instrument Specialist)	Verify the accuracy of the temperature compensator using a resistance standard for instruments having automatic temperature compensation capability. Verify the operation of manual temperature compensators per manufacturer's instructions.

PERSONAL COMPUTERS/DATA SYSTEMS

Equipment	Frequency	Preventative Maintenance Requirements
Personal Computers and Data Systems	Annually (Instrument Specialist)	Carefully clean interior of computer to remove dust.

PURGE AND TRAP UNITS

Equipment	Frequency	Preventative Maintenance Requirements
Purge and Trap Units	Quarterly	Measure the rate of purge gas flow and adjust if necessary.

RADIOCHEMISTRY COUNTERS

Equipment	Frequency	Preventative Maintenance Requirements
Alpha Spectrometers	Daily (Analyst)	Evaluate system performance daily. Performance checks should include a background count, source count rate checks, and a peak resolution check.
	Monthly (Analyst)	Thoroughly clean the sample chamber monthly at a minimum, or when any background increases are observed.
		Visually inspect signal and high voltage cables.
	Quarterly (Analyst)	Check high voltage supplies to determine regular drifts or other factors have caused high voltage to change.
	Semi-Annually (Analyst)	Check time bases for timers.
	Annually (Analyst)	Check ADC/MDC linearity, either integral or differential.
Gamma Spectrometers	Daily (Analyst)	Evaluate system performance. Performance checks should include a background count, count rate checks, and peak resolution check. The count rate and resolution checks should be made, as a minimum, at one high and one low gamma energy. (The preferred gammas are the 0.122 MeV peak of Cobalt-57 and the 1.332 MeV peak of Cobalt-60, as these are the same peaks used for detector specifications.)
	Monthly (Analyst)	Visually inspect signal and high voltage cables and connections.
	Quarterly (Analyst)	Inspect and clean or replace all air filters.

Equipment	Frequency	Preventative Maintenance Requirements
		Check high voltage supplies to determine whether regulator drifts or other factors have caused the high voltage to change.
	Semi-Annually (Analyst)	Thoroughly clean sample chambers to remove any contamination.
		Check time bases for any timers used.
	Annually (Analyst)	Check ADC/MDC linearity, either integral or differential.
Gamma Spectrometers (Continued)	Annually (Analyst) (Continued)	Establish efficiency calibration curves for each geometry routinely used for each system, using an NBS-traceable mixed radionuclide source.
		Calibration curves should also be established whenever the detector is replaced or undergoes a major repair, and whenever daily performance checks reveal unacceptable performance that cannot be resolved through adjustments or minor repairs of electronic modules.
Gas Proportional Counter	Daily (Analyst)	Count alpha and beta background check sources for a predetermined time on a daily basis. Performance checks should include: background in the alpha and beta channels, alpha source counts, and beta source counts.
	Weekly (Analyst)	Calculate cross talk; a significant change is na indication of drift in the discriminator or high voltage settings.
	Monthly (Analyst)	Visually inspect signal and high voltage cables and connections.
	Quarterly (Analyst)	Determine the transmission factors of zero weight planchets for gross alpha and gross beta. Compare to the counter's absolute efficiency.

Equipment	Frequency	Preventative Maintenance Requirements
		Inspect, and clean or replace all air filters.
		Check high voltage supplies to determine whether regulator drifts or other factors have caused the high voltage to change.
	With Each Gas Change (Analyst)	Determine the detector plateau curve quarterly and following any repair of modification to the system. Following a change of counting gas, the plateau curve should either be redetermined or checked at the highest and lowest voltages of the previous plateau.
	Semi-Annually (Analyst)	Check lubrication and alignment of automatic sample changers.
		Clean thoroughly all sample chambers to remove any contamination.
	Annually (Analyst)	Check time, bass for any timers used.
Gas Proportional Counter (Continued)	Annually (Analyst) (Continued)	Prepare self-absorption curves using NBS-traceable sources. In addition, calibrate the system any time the performance check indicates unacceptable operation. Calibration curves should be prepared for both alpha and beta emitters.
Liquid Scintillation Spectrometers	Daily (Analyst)	Count a background vial, or tritium check source and a carbon-14 check source to monitor the system's performance. Take corrective action if unacceptable check is obtained.
	Monthly (Analyst)	Prepare quench correction curves for those procedures using such curves for efficiency correction.
	Quarterly (Analyst)	Inspect, clean or replace all air filters.

Equipment	Frequency	Preventative Maintenance Requirements
	Semi-Annually (Analyst)	Check lubrication and alignment of automatic sample changers.
		Thoroughly clean all sample chambers to remove any contamination.
Scintillation Cell Counters (Radon Emanation Counters)	Daily (Analyst)	Run background and performance count rate check, if not within acceptance limits, trouble-shoot the system.
	Monthly (Analyst)	Clean thoroughly the flask chamber to remove any contamination.
	Semi-Annually (Analyst)	Perform cell calibration using a known standard to determine the cell's percent efficiency. This voltage/count ratio for radium by radon emanation is to be determined semi-annually or whenever anomalous standard recoveries show that the previously determined ratio is no longer valid.
Survey Meters	Semi-Annually (Outside Vendor)	Calibrate each survey meter and probe combination. The use of a meter with a probe other than the one with which it was calibrated constitutes the use of an uncalibrated meter. At a minimum, one calibration count rate meter and one calibrated exposure rate meter will be available at the laboratory at all times. Instruments shipped to the vendor for calibration will be cycled to comply with this requirement.

REFRIGERATION UNITS

Equipment	Frequency	Preventative Maintenance Requirements
Coolers/Freezers	Daily (Surveillance Monitor)	Verify that the operating temperatures are within acceptable limits; record the temperature in the surveillance log.
	Semi-Annually (Facility Maintenance Technician)	Clean inside and outside of unit with detergent. Rinse thoroughly.
		Defrost freezers.

RECORDERS

Equipment	Frequency	Preventative Maintenance Requirements
Recorders	Semi-Annually (Instrument Specialist)	Calibrate those voltage ranges and chart speeds routinely used.

SONICATORS

Equipment	Frequency	Preventative Maintenance Requirements
Sonicators	Daily (Analyst)	Inspect the tip for pitting. Replace as necessary.
		Tune the sonicator according to manufacturer's instructions.

SPECTROPHOTOMETERS

Equipment	Frequency	Preventative Maintenance Requirements
Infrared Spectrometers	Daily (Analyst)	Evaluate the sensitivity and reproducibility of the instrument. When one or both degrades, trouble-shoot the system.
	Quarterly (Analyst)	Run a baseline scan to check beam balance, detector noise, and slit program.
		Run a polystyrene film to check wave length accuracy and sensitivity.
	Annually (Instrument Specialist)	Clean the spectrometer optics. Inspect the chopper belt for wear and replace if necessary.
Turbidimeters	Daily (Analyst)	Evaluate the sensitivity and reproducibility of the instrument during standardization. When one or both characteristics degrade, trouble-shoot the system.
	Annually (Instrument Specialist)	Clean the turbidimeter optics and verify the focusing. Check the range adjustment and adjust if necessary. Visually inspect the printed circuit boards, clean and repair them if necessary.
UV-Visible Spectrometers	Daily (Analyst)	Evaluate sensitivity and reproducibility of instrument during standardization. When one or both characteristics degrade, trouble-shoot the system.
	Monthly (Analyst)	Check for wavelength accuracy, photometric linearity, and stray radiant energy using a set of filters or solutions such as Oxford standards.

Equipment	Frequency	Preventative Maintenance Requirements
	Semi-Annually (Instrument Specialist)	Clean the spectrometer optics semi-annually at a minimum or whenever monthly checks indicate a problem. Visually inspect the printed circuit boards; clean and replace them as necessary.

TITRIMETERS

Equipment	Frequency	Preventative Maintenance Requirements
Titrimeters (Karl Fisher, et. al.)	Daily as required (Analyst)	Check all lines and connections for leaks. Check tubing and cap assembly on reagent bottles for tightness.
		Check for the formation of crystals at connection points and especially in the Teflon stopcocks of the burettes. Remove crystal as described in instrument manual.
		Check the condition of the Dierite^{R}. Regenerate as required.
		Check for cracks or chips on the lip of the reaction vessel. Replace as necessary.
		Check the magnetic latch. Clean as necessary.
	Monthly (Analyst)	Inspect the o-rings under the gland nuts on the cover assembly and the reaction vessel gasket for deterioration. Replace as necessary.
	As Required (Analyst)	Whenever sensitivity declines, remove material coating the tips of the electrodes as described in the instrument manual.

WATER BATHS

Equipment	Frequency	Preventative Maintenance Requirements
Water Baths	Daily (Analyst)	Fill bath with deioized water only to minimize corrosion.
		Clean up any spills in or around water bath.

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LABORATORY METHOD

LOW LEVEL VOLATILE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

METHOD ID: CRA/SN-LLVOA
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

LOW LEVEL VOLATILE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

This method covers the determination of volatile organics in residential water for the Summit National Superfund Site Operation and Maintenance Period project. Reporting limits are listed in Table 1.

2.0 SUMMARY OF METHOD

An inert gas is bubbled through a 25 mL volume of sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeables, which are then detected with a mass spectrometer operating in the electron ionization (EI) mode.

3.0 PROCEDURE

3.1 Sample Preservation

Collect the sample in at least 3 40-mL glass vials with Teflon-lined septa without headspace. Preserve with HCl to pH <2 at sample collection. Store at 1-5 degrees C in a cooler dedicated to VOA sample storage. Complete analysis within 14 days of sample collection.

3.2 Standard Preparation

Stock standards are purchased commercially in sealed ampoules. Depending on the concentration of the purchased solution, intermediate standards may be prepared in methanol, or working standards may be prepared directly from the ampoules. Aliquots of stock solutions are combined as necessary to

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Approvals:

Technical Operations Manager	4/12/94 Date	Quality Assurance Director	4/12/94 Date	Group Leader	4/ Date

prepare intermediate or working standards that contain the analytes of interest. Prepare standard solutions as follows.

3.2.1 Check the expiration date on any stock or intermediate standard to be diluted. Discard material exceeding the expiration date according to waste management procedures.

3.2.2 Determine the appropriate volume of standard material to add to the flask to obtain the desired final concentration as follows:

$$V = (DC/SC) \times FV$$

where V = volume of standard material to be added
DC = desired concentration
SC = standard material concentration
FV = final volume

3.2.4 Fill a volumetric flask just to the neck with dilution solvent.

For gases, remove the entire contents of the ampoule using a syringe and quickly transfer the appropriate amount of standard to the flask to obtain the desired concentration in µg/mL. Use a syringe to add the liquid material directly to the solvent without contacting the neck of the flask. Immerse the needle tip below the surface of the solvent before expelling the solution to reduce evaporation of the standard material. Either partition the remainder of the ampoule into flasks as additional dilutions or discard it. Do not store the remainder because verification of concentration would be required before reuse.

For less volatile analytes, using a syringe and quickly transfer the appropriate amount of standard to the flask to obtain the desired concentration in µg/mL. Use a syringe to add the liquid material directly to the solvent without contacting the neck of the flask. Immerse the needle tip below the surface of the solvent before expelling the solution to reduce evaporation of the standard material.

3.2.5 Add dilution solvent until the bottom of the meniscus reaches the volume mark of the flask using a disposable pipet. Place the tip of the pipet close to the volume mark without immersing it in the dilution solvent. Avoid wetting the neck of the flask above the volume mark.

3.2.6 Stopper the flask and invert three times to mix thoroughly.

3.2.7 Transfer aliquots of intermediate standard solutions to 100-µL vials without headspace using a Pasteur pipet. Label bottles or vials containing standard solutions with the following information:

- Solution name and concentration - use sufficient detail in the description to identify it from other solutions.
- Identification number.
- Date prepared and preparer.
- Expiration date.

3.2.8 Store volatile and semivolatile standard solutions in separate refrigerated storage areas to prevent cross-contamination of standard materials and/or solvents. Store standard solutions in Teflon-sealed containers at $\leq$ 4° C.

3.2.9 Check for minimal to zero headspace in the containers. Mark the meniscus level on any container where headspace in the vial is apparent.

3.2.10 Visually check standard stock solutions prior to use for evidence of degradation or evaporation. Allow the vial to reach room temperature before checking the headspace level.

3.2.11 Replace the solutions sooner than the periods indicated below if degradation or evaporation occurs or if comparison with quality control check samples indicate a problem.

Length of storage periods are as follows:

- Liquid standards - replace monthly.
- Gas standards - replace weekly.

3.3 Instrument Set-up and Tuning

3.3.1 Perform instrument set-up as described below for capillary column operation.

Parameter	Operating Condition
Column Type	Capillary
Column Specifications	105 m, 0.53 mm I.D. or 60 m, 0.53 mm I.D.
Flow Rate/Gas	30 - 40 cm/sec
Column Temperature	**105 m:** 40°C (1 min) to 165°C

at 5°C/min, 165°C to 230°C at 20°C/min.

60 m: 10°C (1 min) to 130°C at 8°C/min, 130°C to 230°C at 20°C/min.

Cryogenic cooling using liquid N_2 is required whenever using the 60 m capillary column.

Trap — Minimum length - 25 cm. Should contain 15 cm of Tenax 60/80 mesh and 8 cm of silica gel 35/60 mesh or equivalent phase.

3.3.2 Tune the instrument as follows:

3.3.2.1 Manually inject 50 ng of BFB and check that the GC/MS system meets the standard mass spectral ion abundance criteria listed below:

Mass	BFB Ion/Abundance Criteria
50	15.0 - 40.0 percent of mass 95
75	30.0 - 60.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	Less than 2.0 percent of mass 174
174	Greater than 50.0 percent of mass 95
175	5.0 - 9.0 percent of mass 174
176	Greater than 95.0 but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

3.3.2.2 Retune the system if criteria are not met. Do not proceed with analysis until a successful tune is performed.

3.3.2.3 Repeat the BFB calibration every 12 hours of operation or

whenever corrective actions are taken that change or affect the tuning criteria (e.g., ion source cleaning or repair). The 12-hour period begins with the BFB injection.

3.4 Initial Calibration

3.4.1 Prepare a 5-point initial calibration curve as follows.

3.4.1.1 Assemble the purge and trap device. Condition the trap initially according to manufacturer's instructions. Prior to daily use, condition the trap for 10 minutes by back-flushing at 180°C with the column at 220°C.

3.4.1.2 Fill a 40-mL VOA vial with 40.0 mL reagent water.

3.4.1.3 Spike target analyte calibration standards into the vial and cap immediately. Spike to achieve standard solutions at 2, 5, 10, 20, and 30 μg/L. Spike with internal standards at 5 μg/L and with surrogates at 10 μg/L.

3.4.1.4 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using the parameters listed in step 3.1.1.

3.4.1.5 Purge the standard for 11.0 $\pm$ 0.1 minutes at ambient temperature for waters and medium level soils, and at 40°C for low level soils.

3.4.1.6 Adjust the device to the desorb mode and begin the GC/MS analysis. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 20 - 60 mL/min for 4 minutes.

3.4.1.7 Desorb for four minutes. Recondition the trap by turning it to the bake mode. Allow the trap to bake at 220°C for 11.0 minutes. Turn off the trap. When cool, the trap is ready for the next standard.

3.4.2 Tabulate the area response of the compound characteristic ions against concentration for each compound and internal standard. Calculate relative response factor (RRF) for each compound using the following equation:

$$RRF = \frac{Ax}{Ais} \times \frac{Cis}{Cx}$$

where Ax = Area of the characteristic ion for the compound to be measured

Ais = Area of the characteristic ion for the specified internal standard (see Table 2)

Cis = Concentration of the internal standard

Cx = Concentration of compound to be measured

3.4.3 Calculate the average Relative Response Factor (RRF_{ave}) for each compound. The RRF_{ave} of the five system performance check compounds (SPCC) listed below must be at least 0.300, with the exception of 0.250 for bromoform.

SPCC

Chloromethane
1,1-Dichloroethane
Bromoform
1,1,2,2-Tetrachloroethane
Chlorobenzene

3.4.4 Calculate the % relative standard deviation (% RSD) of RRF values for each compound. The maximum acceptable % RSD for the calibration check compounds (CCC) listed below is 30%.

CCC

Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

The % RSD is calculated as follows:

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

3.4.5 Once the criteria for initial calibration have been met, report the RRF_{ave} and % RSD for all compounds.

If the SPCC and CCC criteria are not met, evaluate the system and take corrective measures before proceeding with method blank or sample analysis.

3.5 Continuing Calibration

3.5.1 Analyze a 10 µg/L calibration standard containing all target compounds every 12 hours immediately following a successful tune.

3.5.2 The RRF of the five system performance check compounds (SPCC) listed below must be at least 0.300, with the exception of 0.250 for bromoform.

SPCC
Chloromethane
1,1-Dichloroethane
Bromoform
1,1,2,2-Tetrachloroethane
Chlorobenzene

If SPCC criteria are not met, take corrective actions to isolate and correct the problems before continuing with analysis.

3.5.3 Perform a continuing calibration check to verify the validity of the initial calibration by evaluating the % difference of the RRF for calibration check (CCC) compounds.

CCC
Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

Calculate % difference as follows.

$$\% \text{ Difference} = \frac{RRF_{ave} - RRF_c}{RRF_{ave}} \times 100$$

where RRF_{ave} = average response factor from initial calibration.

RRF_c = response factor from current continuing calibration standard

If the % difference for each CCC is $\leq$ 25.0%, assume the initial calibration is valid and continue analysis. If the % difference for any CCC is > 25.0%, take corrective action. f the source of the problem cannot be determined, generate a new five-point initial calibration curve. The calibration criteria must be met before analysis can continue.

Note: If continuing calibration is being performed for a limited set of compounds (e.g., BTEX) sample analysis may proceed as long as % difference is $\leq$ 25.0% and minimum response factor is $\geq$ 0.300 for each target analyte.

3.6 Water Sample Analysis

3.6.1 Repeat step 3.4.1 using 40 mL of sample in place of the calibration standard.

3.6.2 If any compound in the sample exceeds linear calibration range, clean the system by analysis of method blanks until a blank free of interferents is obtained. Reanalyze the sample at a dilution at which no target compound is saturated. Adjust to the final volume with reagent water.

3.6.3 Tabulate the retention time and EICP area for each internal standard against that of the most recent 12-hour continuing calibration standard. If the following criteria are not met, reanalyze the sample:

- The retention time for each internal standard must not change by more than 30 seconds from the latest 12-hour continuing calibration standard.
- The extracted ion current profile (EICP) area for the quantitation ion for each internal standard must not change by more than a factor of two (-50% to +100%) from that of the latest 12-hour continuing calibration standard.

3.6.4 Calculate the surrogate spike recoveries as follows:

$$\text{Percent Surrogate Recovery} = \frac{Qd}{} \times 100$$

Qa

where Qd = quantity determined by analysis
Qa = quantity added to sample

The surrogate spike recoveries must be within the limits listed on Table 3. Acceptable recovery in the method blank must be obtained prior to analyzing the samples. If recovery of a surrogate is outside acceptance limits for a sample, the sample must be reanalyzed.

3.7 Identification of Target Compounds

3.7.1 Identify volatile target compounds by comparison of the sample and standard mass spectra generated during a 12-hour period.

3.7.2 Positively identify a compound by meeting the following criteria:

- The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the standard component.
- All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified in the above paragraph must agree within ± 20% absolute intensity between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data enhancement programs are used to obtain the sample component spectrum, both the enhanced and the raw spectra must be evaluated. The verification process should favor false negatives.

3.8 Quantitation of Target Compounds

3.8.1 Quantify target components identified by the internal standard method. The internal standard nearest the retention time of a given analyte is used for quantitation (see Table 2).

3.8.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the response factor as determined in step 3.4.2 and the following equations:

Note: Since o- and p-xylene overlap on the packed column, the

xylenes must be quantitated as m-xylene. Likewise, since m- and p-xylenes coelute on the capillary column, the xylenes must be reported as o-xylene. The concentration of all xylene isomers must be added together and the result reported as total xylenes.

$$\text{Concentration (in } \mu\text{g/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specified internal standard

I_s = Amount of internal standard added in ng

V_o = Volume of water purged in mL (take into account any dilutions)

4.0 DATA COLLECTION

4.1.1 Document all data in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. Examples of appropriate forms for data collection (i.e., assignment sheets and injection log) are shown on Figures 1-3.

Data collection should include the following:

- method code and brief description (e.g., 25-mL Purge VOA).
- instrument parameters.
- date and time of BFB injection, and analyst(s) signature(s).
- lab sample number and aliquot, and data system filename. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added.

4.1.2 Forward the following to data management from each 12-hour tune for data package preparation:

- description of problems encountered and actions taken during sample

analysis on corrective action records

- initial and continuing calibration files
- tune files
- sample and associated quality control sample files (method blank, lab control standard, MS/MSD)
- chromatograms, quantitation reports, and mass spectra for samples and associated quality control samples
- logbook page(s) and assignment sheets

5.0 QUALITY CONTROL

5.1 Method Blank Analysis

Run a method blank analysis every 12 hours immediately following a successful initial or continuing calibration as follows. Analyze an aliquot of reagent water according to the procedure described in Section 3.4.

A method blank must not contain more than five times the reporting limit of the following common laboratory solvents: methylene chloride, acetone and 2-butanone.

Evaluate internal standard response and retention times and surrogate spike recoveries as described in Sections 3.6.3 and 3.6.4. These criteria must be met prior to proceeding with sample analysis.

5.2 Lab Control Standard (LCS)

Prepare and analyze an LCS each day samples are run. Spike an aliquot of reagent water with 8 μL of the matrix spiking solution, and perform VOA analysis.

Recovery of at least 12 of the 13 LCS compounds the surrogate standard compounds must meet the must meet the limits listed in Table 3. If the recovery of 2 or more LCS compounds or 1 surrogate compound is unacceptable, troubleshoot the GC/MS system and/or standards and obtain acceptable LCS recovery before proceeding with analysis.

5.3 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

Prepare and analyze an MS/MSD with every twenty samples of similar matrix and concentration. Take two additional aliquots of the selected sample(s), spiked with 8 μL of the matrix spiking solution, and perform VOA analysis.

When a sample requiring dilution has been chosen as the MS/MSD, the MS/MSD must be analyzed at the same dilution as the unspiked sample. Calculate percent recovery as follows:

$$\text{Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Calculate the relative % difference (RPD) as follows:

$$RPD = \frac{2(D_1 - D_2)}{(D_1 + D_2)} \times 100$$

where D_1 = MS Result
D_2 = MSD Result

Advisory MS/MSD percent recovery and RPD limits are listed on Table 3. Since these limits are for advisory purposes only, they are not used to determine if sample reanalysis is required.

5.4 METHOD DETECTION LIMIT STUDIES

A method detection limit (MDL) study is performed annually according to 40 CFR 136, Appendix B. Statistically-based MDLs must be less than or equal to the reporting limit.

5.5 CONTROL LIMITS

The statistically-based limits for precision and accuracy listed in Table 3 are updated periodically and, therefore, subject to change.

6.0 INTERFERENCES

6.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method blanks. Use TFE-tubing and TFE-thread sealants. Avoid using flow controllers with rubber components in the purging device.

6.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal during storage

and handling.

6.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross-contamination.

6.4 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to flush the purging device with a detergent solution, rinse it with distilled water, and dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; frequent bakeout and purging of the entire system may be required.

7.0 SAFETY PRECAUTIONS

7.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

7.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.2 Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDS).

7.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.4 Handle all glass equipment with care, particularly during assembly and disassembly.

7.5 Avoid contact with hot GC parts (e.g., injection ports or transfer lines).

7.6 Vent GC/MS mechanical pump exhaust to the outside.

8.0 APPARATUS AND MATERIALS

8.1 Micro syringes: 5-μL and larger, 0.006 inch ID needle.

8.2 Syringe valve: Two-way valve with Luer-lock ends (3-inch), if applicable to the purging device.

8.3 Syringe: 5.0-mL, gas tight with shut-off valve.

8.4 Analytical Balance: Capable of weighing to 0.0001 g.

8.5 VOA vials: 40-mL, screw cap with teflon liner.

8.6 Flasks: Class A, volumetric with ground glass stoppers.

8.7 GC column: 105 m x 0.53 mm ID Rtx Volatiles or 60 m x 0.53 mm ID Rtx 502.2, or equivalent.

8.8 Purge and trap device: TEKMAR/LSC-2, Tekmar Model 4000/ALS or equivalent.

8.9 Gas Chromatograph/Mass Spectrometer (GC/MS): Finnigan 4023/9610, Finnigan Incos 50B or equivalent.

8.10 GC/MS Data System: Finnigan MAT-1 Incos or equivalent. System equipped with Super Incos software.

8.11 Autosampler: Dynatech PTA 30W or PTA 30W/S or equivalent. Calibrate the sample loop of each unit following installation.

8.12 Vials: 2-mL glass with Teflon-sealed screw caps.

8.13 Volumetric Flasks: 5-mL and 10-mL capacity with ground glass stoppers.

9.0 REAGENTS

9.1 Reagent water: Deionized water passed through an activated carbon column.

9.2 Sodium thiosulfate: Granular, ACS grade.

9.3 Methanol: Pesticide quality or equivalent.

9.4 Stock standard solutions: Prepare from pure standard materials or purchase commercially; prepare stock standard solutions in methanol using assayed liquids or gases as appropriate.

9.5 Calibration Standards: Prepare calibration standards for each priority pollutant and TCL compound at five concentration levels from stock solutions: 2, 5, 10, 20, and 30 µg/L. Alternatively, varying amounts of a TCL composite standard may be used to obtain each of these concentrations.

9.6 Surrogate, Internal and Matrix Spiking Standard Solutions:

9.6.1 **Surrogate and Internal Standards** - Prepare solutions containing surrogate and internal standards at a concentrations of 125 and 250 µg/mL of each compound in methanol.

9.6.2 **4-Bromofluorobenzene (BFB) Standard** - Prepare a 50 µg/mL solution of BFB in methanol.

9.6.3 **LCS/Matrix Spiking Solution** - Prepare a solution containing the following compounds in methanol.

Benzene	25 ug/L
Chlorobenzene	25 ug/L
Chloroform	25 ug/L
Chloromethane	25 ug/L
1,1-Dichloroethane	25 µg/L
1,1-Dichloroethene	25 ug/L
1,2-Dichloropropane	25 ug/L
Ethylbenzene	25 ug/L
Methylbenzene [toluene]	25 ug/L
1,1,2,2-Tetrachloroethane	25 ug/L
Trichloroethene	25 µg/L
Tribromomethane [bromoform]	25 ug/L
Vinyl Chloride	25 ug/L

10.0 REFERENCES

U.S. EPA SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Volume IB, 1986, Method 8260.

TABLE 1

Volatile Organics Reporting Limits for Residential Well Analyses

Parameter	Water ug/L
chloromethane	1
bromomethane	1
vinyl chloride	1
chloroethane	1
methylene chloride	1
acetone	2
carbon disulfde	1
1,1-dichloroethene	1
1,1-dichloroethane	1
1,2-dichloroethene (total)	1
chloroform	1
1,2-dichloroethane	1
2-butanone	2
1,1,1-trichloroethane	1
carbon tetrachloride	1
bromodichloromethane	1
1,2-dichloropropane	1
cis-1,3-dichloropropene	1
trichloroethene	1
dibromochloromethane	1
1,1,2-trichloroethane	1
benzene	1
trans-1,3-dichloropropene	1
bromoform	1
4-methyl-2-pentanone	1
2-hexanone	2
tetrachloroethene	1

TABLE 1
Volatile Organics Reporting Limits for Residential Well Analyses
Page Two

Parameter	Water ug/L
toluene	1
1,1,2,2-tetrachloroethane	1
chlorobenzene	1
ethylbenzene	1
styrene	1
xylenes (total)	1

TABLE 2

Internal Standard Assignments

Bromochloromethane:	1,4-Difluorobenzene:	Chlorobenzene:
1,2-dichloroethane-d4	vinyl acetate	4-methyl-2-pentanone
chloromethane	1,1,1-trichloroethane	toluene
vinyl chloride	carbon tetrachloride	tetrachloroethene
bromomethane	benzene	2-hexanone
chloroethane	trichloroethene	chlorobenzene
1,1-dichloroethene	1,2-dichloropropane	ethylbenzene
acetone	bromodichloromethane	xylenes
carbon disulfide	2-chloroethylvinyl ether	styrene
methylene chloride	cis-1,3-dichloropropene	1,1,2,2-tetrachloroethane
trans-1,2-dichloroethene	trans-1,3-dichloropropene	
1,1-dichloroethane	1,1,2-trichloroethane	
2-butanone	dibromochloromethane	
chloroform	bromoform	
acrolein		
acrylonitriletrichlorofluoromethane		
dichlorodifluoromethane		
cis-1,2-dichloroethene		

TABLE 3

GC/MS VOA Control Limits

QUALITY CONTROL TEST FILE
VOLATILE ORGANICS - GC/MS
WATER
PM: 00; AM: 020W

COMPOUND	COMBO	PRECISION AS RPD					PERCENT RECOVERY OF LAB CONTROL STANDARDS					PERCENT RECOVERY OF MATRIX SPIKES			
		WL	CL	X	S	CPK[1]	WL	CL	X	S	CPK[2]	95% CI	99% CI	X	S
1,1,1-trichloroethane	0850	≤12.3	≤16.2	4.40	3.93		79.9-111	72.0-119	95.66	7.88		79.6-116	70.5-126	98.01	9.18
1,1,2,2-tetrachloroethane	0C01	≤13.5	≤17.9	4.72	4.39		75.0-114	65.2-124	94.79	9.87		82.4-113	74.7-121	97.70	7.67
1,1,2-trichloroethane	0C03	≤11.6	≤15.4	4.21	3.72		83.4-115	75.5-123	99.04	7.84		84.7-114	77.3-122	99.56	7.43
1,1-dichloroethane	0C04	≤9.06	≤11.5	4.22	2.42		81.4-118	72.2-127	99.76	9.18		85.0-116	77.2-124	100.71	7.83
1,1-dichloroethene	0C05	≤11.3	≤14.9	4.18	3.58		67.4-129	52.1-144	97.95	15.29		59.3-131	41.5-149	95.04	17.86
1,2-dichloroethane	0C14	≤9.28	≤12.1	3.64	2.82		75.8-119	65.1-129	97.29	10.73		83.3-118	74.6-127	100.6	8
1,2-dichloropropane	0C16	≤10.1	≤13.3	3.89	3.13		77.1-115	67.6-124	96.00	9.45		86.2-114	79.3-121	99.93	6.87
2-butanone (MEK)	0C29	≤46.3	≤62.6	13.67	16.3		57.8-129	40.0-147	93.49	17.82		-	-	-	-
2-chloroethylvinyl ether	0C31	≤10.9	≤14.6	3.44	3.71		53.9-124	36.3-142	89.18	17.62[3]		51.9-133	31.6-153	92.43	20.26
2-hexanone	0C32	≤17.8	≤23.6	6.23	5.80		60.3-119	45.6-134	89.78	14.73		-	-	-	-
4-methyl-2-pentanone (MIBK)	0C38	≤14.3	≤19.2	4.51	4.91		62.8-125	47.1-141	94.11	15.68		-	-	-	-
acetone	0C40	≤30.9	≤40.7	11.29	9.80		56.5-136	36.5-156	96.32	19.93		-	-	-	-
benzene	0C44	≤9.22	≤12.1	3.42	2.90		79.4-111	71.5-119	95.07	7.85		80.4-122	70.0-133	101.28	10.42
bromodichloromethane	0C46	≤9.50	≤12.5	3.43	3.04		80.3-114	71.9-122	97.00	8.37		91.2-108	87.0-112	99.71	4.25
bromomethane	0C47	≤14.4	≤18.5	6.25	4.07		67.2-136	50.1-153	101.57	17.16		76.2-124	64.2-136	100.01	11.93
carbon disulfide	0C48	≤20.2	≤26.2	8.10	6.03		48.8-135	27.3-156	91.67	21.45		-	-	-	-
carbon tetrachloride	0C49	≤12.1	≤15.8	4.65	3.72		74.5-114	64.6-124	94.47	9.97		70.4-115	59.4-126	92.48	11.02
chlorobenzene	0C50	≤8.92	≤11.9	3.04	2.94		83.3-112	76.2-119	97.48	7.10		78.2-126	66.4-138	101.95	11.85
chloroethane	0D01	≤15.5	≤19.9	6.71	4.39		66.6-130	50.7-146	98.35	15.88		69.6-122	56.4-136	95.98	13.21
chloroform	0D02	≤8.07	≤10.5	3.14	2.46		78.7-119	68.6-129	98.86	10.07		69.3-130	54.2-145	99.53	15.12
chloromethane	0D03	≤15.3	≤19.8	6.32	4.50		64.6-125	49.6-140	94.76	15.07		61.1-140	41.3-160	100.55	19.74
cis-1,3-dichloropropene	0D05	≤10.1	≤13.4	3.72	3.21		78.1-110	70.2-117	93.83	7.86		84.2-110	77.8-116	96.94	6.39

TABLE 3
GC/MS VOA Control Limits (cont'd)
Page Two

QUALITY CONTROL TEST FILE
VOLATILE ORGANICS - GC/MS
WATER
PM: 00; AM: 0204

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
dibromochloromethane	0008	≤10.5	≤13.9	3.84[3]	3.34[3]		82.1-115	73.9-123	98.41	8.16		81.1-117	72.1-126	99.20	9.03
dichloromethane (methylene chloride)	0013	≤16.2	≤21.4	5.69[3]	5.25[3]		79.2-117	69.8-127	98.18	9.47		83.4-127	72.6-137	104.98	10.80
ethylbenzene	0018	≤8.37	≤11.0	3.18[3]	2.60[3]		83.1-110	76.4-116	96.42	6.67		75.7-117	65.4-127	96.34	10.31
methylbenzene(toluene)	0032	≤11.5	≤15.5	3.59	3.96		79.4-112	71.2-121	95.94	8.25		76.6-118	66.2-128	97.27	10.36
styrene	0040	≤11.7	≤15.7	3.81[3]	3.97[3]		83.9-110	77.5-116	96.76	6.43		-	-	-	-
tetrachloroethene	0041	≤10.8	≤14.3	3.80[3]	3.50[3]		64.2-123	49.5-138	93.65	14.71		44.7-136	21.8-159	90.50	22.91
trans-1,2-dichloroethene		≤9.90	≤12.9	3.89[3]	3.01[3]				98.29[3]	8.46[3]		-	-	-	-
trans-1,3-dichloropropene	0044	≤7.63	≤9.90	3.10[3]	2.27[3]		77.9-110	69.7-119	94.18	8.16		76.1-110	67.5-119	93.22	8.58
tribromomethane(bromoform)	0046	≤12.6	≤16.7	4.48[3]	4.08[3]		81.0-110	73.9-117	95.38	7.17		75.8-111	67.1-120	93.35	8.76
trichloroethene	0047	≤9.83	≤13.1	3.25	3.29		76.0-115	66.2-125	95.69	9.83		70.9-127	56.9-141	98.74	13.94
vinyl acetate	0E01	≤13.5	≤17.7	5.02[3]	4.23[3]		60.3-125	44.1-142	92.84	16.26		-	-	-	-
vinyl chloride	0E02	≤19.6	≤25.2	8.55[3]	5.55[3]		69.7-125	55.8-139	97.56	13.91		34.5-140	8.16-166	87.18	26.34
xylenes, total	0E03	≤10.8	≤14.2	3.78[3]	3.49[3]		82.5-112	75.2-119	97.17	7.33		-	-	-	-
1,2-dichloroethane-d4 (S)	0C15	NA	NA	NA	NA	NA	83.0-114	75.2-122	98.68	7.83		NA	NA	NA	NA
4-bromofluorobenzene (S)	0C37	NA	NA	NA	NA	NA	91.6-108	87.4-112	99.93	4.18		NA	NA	NA	NA
toluene-d8 (S)	0D42	NA	NA	NA	NA	NA	91.2-113	85.8-118	101.89	5.37		NA	NA	NA	NA

FIGURE 1

GCMS Assignment Sheet (29-Jul-92 Samples 206415 - 206416)

Due Date: ___-___-___

Date entered and init.: ___-___-___ _____
Approved and init.: ___-___-___ _____

Sample: P206416 Test: OVFPV Type: SRIG
Analysis Number: 2 Anls. Ref. Number:
Analyst (Empl) Number: _____
Date Analyzed: ___-___-___ Time: _____
Instrument: GCMS _____
Book: _____-_____ Page: _____
Sample Description: S/S HALOCLEAN SUMP / ZONE EXT
Client: ___
UNITS: _____ BLANK SAMPLE #: _____

Run File | Dilution | Lab Page | Anlst/Processor(Empl)

Time Sampled: | Received 17-JUL-92 | Original (vol/wt): _____ | Final (vol): _____
RUN BATCH #: _____ Prep Meth: 00 Anls Meth: 0200E-
CASE ID: Not Available SDG: Not Available

VOLATILES

ANALYTE	DETECTION LIMIT	RESULT	QUALIFIER
1,1,1-Trichloroethane			
1,1,2,2-Tetrachloroethane			
1,1,2-Trichloroethane			
1,1-Dichloroethane			
1,1-Dichloroethene			
1,2-Dichloroethane			
1,2-Dichloroethene (total)			
1,2-Dichloropropane			
2-Chloroethylvinylether			
Acrolein			
Acrylonitrile			
Benzene			
Bromoform			
Bromomethane			
Carbon tetrachloride			
Chlorobenzene			
Chlorodibromomethane			
Chloroethane			
Chloroform			
Chloromethane			
Dichlorobromomethane			
Ethylbenzene			
Methylene chloride			
Tetrachloroethene			
Toluene			
Trichloroethene			
Vinyl chloride			
cis-1,3-Dichloropropene			
trans-1,3-Dichloropropene			

SURROGATES

1,2-Dichloroethane-d4			
4-Bromofluorobenzene			
Toluene-d8			

EXAMPLE ONLY

COMMENTS: _____

Special Instructions

P206416 TYPE C

FIGURE 2

Halliburton NUS Laboratory Services Group--Pittsburgh

VOLATILE ORGANIC GC/MS ANALYSIS Notebook #:

Date:

Level: Low /Medium Matrix: Water /Soil /Other

Client:

		STANDARDS:
PARAMETERS	He flow:	bfb:
Column:	Col. head pressure:	is/su:
Prog:	(inj. #):	hsl:
Source temp:	Cylinder Pressures:	gas:
Trans. temp:	He carrier:	extras:
Inj. temp:	air/H2:	
Sep. temp:	He purge:	
Initial Cali:	Trap #:	Temp. tape:

Run#	File name	Ident	Dilution	Libr	Comments	Perm Tape

EXAMPLE ONLY

Comments:

Analyst :

Date:

Reviewer:

Date:

FIGURE 3

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CORPORATION

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LABORATORY METHOD

VOLATILE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

METHOD ID: CRA/SN-VOA
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

VOLATILE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

This method covers the determination of priority pollutant and US EPA CLP target compound list (TCL) purgeable organics in water and sediment/soil for the Summit National Superfund Site Operation and Maintenance Period project. Reporting limits are listed in Table 1.

2.0 SUMMARY OF METHOD

Water Samples

An inert gas is bubbled through a volume of sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeables, which are then detected with a mass spectrometer operating in the electron ionization (EI) mode.

Sediment/Soil Samples

Low Level

An inert gas is bubbled through a sample/water mixture held at 40°C in a specially designed purging chamber. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature-programmed to separate the purgeables, which are then detected with a mass spectrometer.

Approvals:

Technical Operations Manager	4/12/94 Date	Quality Assurance Director	4/12/94 Date	Group Leader	4/12/94 Date

Medium Level

A measured amount (usually 4 g) of soil is extracted with 10 mL methanol. A portion (usually 100 µL) of the methanol extract is diluted to 5 mL with reagent water. At this point the sample is processed in the same manner as described above for water samples.

3.0 PROCEDURE

3.1 Sample Preservation

3.1.1 Water

Collect the sample in 3 40-mL glass vials with Teflon-lined septa without headspace. Preserve with HCl to pH <2 at sample collection. Store at 1-5 degrees C in a cooler dedicated to VOA sample storage. Complete analysis within 14 days of sample collection.

3.1.2 Soil

Collect sample in vial labeled for VOA analysis. Minimize headspace. Store at 1-5 degrees C in a cooler dedicated to VOA sample storage. Complete analysis within 14 days of sample collection.

3.2 Standard Preparation

Stock standards are purchased commercially in sealed ampoules. Depending on the concentration of the purchased solution, intermediate standards may be prepared in methanol, or working standards may be prepared directly from the ampoules. Aliquots of stock solutions are combined as necessary to prepare intermediate or working standards that contain the analytes of interest. Prepare standard solutions as follows.

3.2.1 Check the expiration date on any stock or intermediate standard to be diluted. Discard material exceeding the expiration date according to waste management procedures.

3.2.2 Determine the appropriate volume of standard material to add to the flask to obtain the desired final concentration as follows:

$$V = (DC/SC) \times FV$$

where V = volume of standard material to be added
DC = desired concentration
SC = standard material concentration
FV = final volume

3.2.4 Fill a volumetric flask just to the neck with dilution solvent.

For gases, remove the entire contents of the ampoule using a syringe and quickly transfer the appropriate amount of standard to the flask to obtain the desired concentration in µg/mL. Use a syringe to add the liquid material directly to the solvent without contacting the neck of the flask. Immerse the needle tip below the surface of the solvent before expelling the solution to reduce evaporation of the standard material. Either partition the remainder of the ampoule into flasks as additional dilutions or discard it. Do not store the remainder because verification of concentration would be required before reuse.

For less volatile analytes, using a syringe and quickly transfer the appropriate amount of standard to the flask to obtain the desired concentration in µg/mL. Use a syringe to add the liquid material directly to the solvent without contacting the neck of the flask. Immerse the needle tip below the surface of the solvent before expelling the solution to reduce evaporation of the standard material.

3.2.5 Add dilution solvent until the bottom of the meniscus reaches the volume mark of the flask using a disposable pipet. Place the tip of the pipet close to the volume mark without immersing it in the dilution solvent. Avoid wetting the neck of the flask above the volume mark.

3.2.6 Stopper the flask and invert three times to mix thoroughly.

3.2.7 Transfer aliquots of intermediate standard solutions to 100-µL vials without headspace using a Pasteur pipet. Label bottles or vials containing standard solutions with the following information:

- Solution name and concentration - use sufficient detail in the description to identify it from other solutions.
- Identification number.
- Date prepared and preparer.
- Expiration date.

3.2.8 Store volatile and semivolatile standard solutions in separate refrigerated storage areas to prevent cross-contamination of standard materials and/or solvents. Store standard solutions in Teflon-sealed containers at $\leq 4°$ C.

3.2.9 Check for minimal to zero headspace in the containers. Mark the meniscus level on any container where headspace in the vial is apparent.

3.2.10 Visually check standard stock solutions prior to use for evidence of degradation or evaporation. Allow the vial to reach room temperature before checking the headspace level.

3.2.11 Replace the solutions sooner than the periods indicated below if degradation or evaporation occurs or if comparison with quality control check samples indicate a problem.

Length of storage periods are as follows:

- Liquid standards - replace monthly.
- Gas standards - replace weekly.

3.3 Instrument Set-up and Tuning

3.3.1 Perform instrument set-up as described below for capillary column operation.

Parameter	Operating Condition
Column Type	Capillary
Column Specifications	105 m, 0.53 mm I.D. or 60 m, 0.53 mm I.D.
Flow Rate/Gas	30 - 40 cm/sec
Column Temperature	**105 m:** 40°C (1 min) to 165°C at 5°C/min, 165°C to 230°C at 20°C/min. **60 m:** 10°C (1 min) to 130°C at 8°C/min, 130°C to 230°C at 20°C/min. Cryogenic cooling using liquid N_2 is required whenever using the 60 m capillary column.
Trap	Minimum length - 25 cm. Should contain 15 cm of Tenax 60/80 mesh and 8 cm of silica gel 35/60 mesh or equivalent phase.

3.3.2 Tune the instrument as follows:

3.3.2.1 Manually inject 50 ng of BFB and check that the GC/MS system meets the standard mass spectral ion abundance criteria listed below:

Mass	BFB Ion/Abundance Criteria
50	15.0 - 40.0 percent of mass 95
75	30.0 - 60.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95
173	Less than 2.0 percent of mass 174
174	Greater than 50.0 percent of mass 95
175	5.0 - 9.0 percent of mass 174
176	Greater than 95.0 but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

3.3.2.2 Retune the system if criteria are not met. Do not proceed with analysis until a successful tune is performed.

3.3.2.3 Repeat the BFB calibration every 12 hours of operation or whenever corrective actions are taken that change or affect the tuning criteria (e.g., ion source cleaning or repair). The 12-hour period begins with the BFB injection.

3.4 Initial Calibration

3.4.1 Prepare a 5-point initial calibration curve as follows. Perform separate initial calibrations for waters (ambient temperature purge), low level soils (40°C purge) and medium level soils (ambient temperature purge with methanol added).

3.4.1.1 Assemble the purge and trap device. Condition the trap initially according to manufacturer's instructions. Prior to daily use, condition the trap for 10 minutes by back-flushing at 180°C with the column at 220°C.

3.4.1.2 Fill a 16-mL screw cap autosampler vial with 10 mL reagent water for the "W/S" autosamplers and 15 mL reagent water for the "W" unit.

3.4.1.3 Spike target analyte calibration standards into the vial and cap immediately. Spike to achieve standard solutions at 20, 50, 100, 150 and 200 µg/L. For medium level soil calibrations, add 100 µL methanol.

3.4.1.4 Load the autosampler with the appropriate internal standard/surrogate spiking solution. The 125 µg/mL solution is used for systems C and D; the 250 µg/mL solution is used for system E. (The difference is due to the internal standard sample loop in each system.) The auto sampler will spike each standard, sample and blank with the solution (2.0 µL for systems C and D; 1.0 µL for system E).

3.4.1.5 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using the parameters listed in step 3.1.1.

3.4.1.6 Purge the standard for 11.0 ± 0.1 minutes at ambient temperature for waters and medium level soils, and at 40°C for low level soils.

3.4.1.7 Adjust the device to the desorb mode and begin the GC/MS analysis. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 20 - 60 mL/min for 4 minutes.

3.4.1.8 Desorb for four minutes. Recondition the trap by turning it to the bake mode. Allow the trap to bake at 220°C for 11.0 minutes. Turn off the trap. When cool, the trap is ready for the next standard.

3.4.2 Tabulate the area response of the compound characteristic ions against concentration for each compound and internal standard. Calculate relative response factor (RRF) for each compound using the following equation:

$$RRF = \frac{Ax}{Ais} \times \frac{Cis}{Cx}$$

where Ax = Area of the characteristic ion for the compound to be measured

Ais = Area of the characteristic ion for the specified internal standard (see Table 2)

Cis = Concentration of the internal standard

Cx = Concentration of compound to be measured

3.4.3 Calculate the average Relative Response Factor (RRF_{ave}) for each compound. The RRF_{ave} of the five system performance check compounds (SPCC) listed below must be at least 0.300, with the exception of 0.250 for bromoform.

SPCC
Chloromethane
1,1-Dichloroethane
Bromoform
1,1,2,2-Tetrachloroethane
Chlorobenzene

3.4.4 Calculate the % relative standard deviation (% RSD) of RRF values for each compound. The maximum acceptable % RSD for the calibration check compounds (CCC) listed below is 30%.

CCC
Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

The % RSD is calculated as follows:

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

3.4.5 Once the criteria for initial calibration have been met, report the RRF_{ave} and % RSD for all compounds.

If the SPCC and CCC criteria are not met, evaluate the system and take corrective measures before proceeding with method blank or sample analysis.

3.5 Continuing Calibration

3.5.1 Analyze a 50 µg/L calibration standard containing all target compounds every 12 hours immediately following a successful tune.

3.5.2 The RRF of the five system performance check compounds (SPCC) listed below must be at least 0.300, with the exception of 0.250 for bromoform.

SPCC

Chloromethane
1,1-Dichloroethane
Bromoform
1,1,2,2-Tetrachloroethane
Chlorobenzene

If SPCC criteria are not met, take corrective actions to isolate and correct the problems before continuing with analysis.

3.5.3 Perform a continuing calibration check to verify the validity of the initial calibration by evaluating the % difference of the RRF for calibration check (CCC) compounds.

CCC

Vinyl chloride
1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene

Calculate % difference as follows.

$$\% \text{ Difference} = \frac{RRF_{ave} - RRF_c}{RRF_{ave}} \times 100$$

where RRF_{ave} = average response factor from initial calibration.

RRF_c = response factor from current continuing calibration standard

If the % difference for each CCC is $\leq$ 25.0%, assume the initial calibration is valid and continue analysis. If the % difference for any CCC is > 25.0%, take corrective action. f the source of the problem cannot be determined, generate a new five-point initial calibration curve. The calibration criteria must be met before analysis can continue.

Note: If continuing calibration is being performed for a limited set of compounds (e.g., BTEX) sample analysis may proceed as long as % difference is $\leq$ 25.0% and minimum response factor is $\geq$ 0.300 for each target analyte.

3.6 Water Sample Analysis

3.6.1 Repeat step 3.4.1 using 10 or 15 mL of sample in place of the calibration standard.

3.6.2 If any compound in the sample exceeds linear calibration range, clean the system by analysis of method blanks until a blank free of interferents is obtained. Reanalyze the sample at a dilution at which no target compound is saturated. Adjust to the final volume with reagent water.

3.6.3 Tabulate the retention time and EICP area for each internal standard against that of the most recent 12-hour continuing calibration standard. If the following criteria are not met, reanalyze the sample:

- The retention time for each internal standard must not change by more than 30 seconds from the latest 12-hour continuing calibration standard.
- The extracted ion current profile (EICP) area for the quantitation ion for each internal standard must not change by more than a factor of two (-50% to +100%) from that of the latest 12-hour continuing calibration standard.

3.6.4 Calculate the surrogate spike recoveries as follows:

$$\text{Percent Surrogate Recovery} = \frac{Qd}{Qa} \times 100$$

where Qd = quantity determined by analysis
Qa = quantity added to sample

The surrogate spike recoveries must be within the limits listed on Table 3. Acceptable recovery in the method blank must be obtained prior to analyzing the samples. If recovery of a surrogate is outside acceptance limits for a sample, the sample must be reanalyzed.

3.7 Soil/Sediment/Waste Sample Analysis

Note: Determine the method to use as follows or alternatively, screen all soil/sediments by the medium level protocol:

- Analyze the sample as a medium level soil/sediment if solvent vapor or oily material is observed.

- Analyze the sample as a low level soil/sediment if solvent vapor is not observed.

3.7.1 Analyze low level soil/sediment/waste samples as follows:

3.7.1.1 Do not discard any supernatant liquid. Mix the contents of the sample container with a metal spatula.

3.7.1.2 Tare a 40-mL VOA vial and weigh 5.0 gm of sample into it. Record the amount in the vial.

Note: If peaks are saturated from the analysis of a 5.0 gm sample, analyze a smaller sample aliquot to prevent saturation. However, the smallest sample aliquot permitted is 1.0 gm. If less than 1.0 gm is needed, the medium level method must be used.

3.7.1.3 Add 5.0 mL of reagent water and 5.0 μL of the surrogate/internal standard spiking solution to the vial.

3.7.1.4 Connect the 40-mL VOA vial to the purge and trap system. Heat the sample to 40°C ± 1°C and proceed with the analysis as described in steps 3.2.1d-g.

Evaluate internal standard responses and retention times and surrogate spike recoveries as described in Sections 3.6.3 and 3.6.4.

3.7.2 Analyze medium level soil/sediment/waste samples as follows:

3.7.2.1 Do not discard any supernatant liquid. Mix the contents of the sample container with a metal spatula.

3.7.2.2 Tare a 40-mL VOA vial and weigh 4.0 gm into it. Record the amount in the vial.

3.7.2.3 Quickly add 9.0 mL of methanol followed by 1.0 mL of surrogate spiking solution to the vial, cap, and shake for 2 minutes.

Note: Perform these additions rapidly to avoid loss of volatiles.

3.7.2.4 Allow the extract to settle for 2 minutes (approx.) and remove 1-2 mL of the methanol solution to a 2-mL screw cap vial with a teflon-lined septa. Label with "MLS" and sample number. Use on the same day.

3.7.2.5 Add 100 µL of the methanol extract and 5.0 µL of internal standard spiking solution to 4.9 mL of reagent water. Inject the water/methanol sample into the purging chamber and proceed with the analysis as described in steps 3.2.1d-g.

Evaluate internal standard responses and retention times and surrogate spike recoveries as described in Sections 3.6.3 and 3.6.4.

3.8 Identification of Target Compounds

3.8.1 Identify volatile target compounds by comparison of the sample and standard mass spectra generated during a 12-hour period.

3.8.2 Positively identify a compound by meeting the following criteria:

- The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the standard component.
- All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified in the above paragraph must agree within ± 20% absolute intensity between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer data enhancement programs are used to obtain the sample component spectrum, both the enhanced and the raw spectra must be evaluated. The verification process should favor false negatives.

3.9 Quantitation of Target Compounds

3.9.1 Quantify target components identified by the internal standard method. The internal standard nearest the retention time of a given analyte is used for quantitation (see Table 2).

3.9.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the response factor as determined in step 3.4.2 and the following equations:

Note: Since o- and p-xylene overlap on the packed column, the xylenes must be quantitated as m-xylene. Likewise, since m- and p-xylenes coelute on the capillary column, the xylenes must be reported as o-xylene. The concentration of all xylene isomers must be added together and the result reported as total xylenes.

3.9.2.1 Water samples

$$\text{Concentration (in } \mu\text{g/L)} = \frac{(A_x)\,(I_s)}{(A_{is})(RF)(V_o)}$$

where A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specified internal standard

I_s = Amount of internal standard added in ng

V_o = Volume of water purged in mL (take into account any dilutions)

3.9.2.2 Medium level sediment/soil samples

$$\text{Concentration (in } \mu\text{g/kg)} = \frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

3.9.2.3 Low level sediment/soil samples

$$\text{Concentration (in } \mu\text{g/kg)} = \frac{(A_x)\,(I_s)}{(A_{is})(RF)(W_s)}$$

where A_x, I_s, A_{is} = same as above

V_t = Volume of total extract in μL (use 10,000 μ/L or a factor of this when dilutions are made)

V_i = Volume of extract added in μL for purging

W_s = Wet weight of sample purged in gm

4.0 DATA COLLECTION

4.1.1 Document all data in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. Examples of appropriate forms for data collection (i.e., assignment sheets and injection log) are shown on Figures 1-3.

Data collection should include the following:

- method code and brief description (e.g., GC/MS - LLW).
- instrument parameters.
- date and time of BFB injection, and analyst(s) signature(s).
- lab sample number and aliquot, and data system filename. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added.

4.1.2 Forward the following to data management from each 12-hour tune for data package preparation:

- description of problems encountered and actions taken during sample analysis on corrective action records
- initial and continuing calibration files
- tune files
- sample and associated quality control sample files (method blank, lab control standard, MS/MSD)
- chromatograms, quantitation reports, and mass spectra for samples and associated quality control samples
- logbook page(s) and assignment sheets

5.0 QUALITY CONTROL

5.1 Method Blank Analysis

Run a method blank analysis every 12 hours immediately following a successful initial or continuing calibration as follows.

5.1.1 Low Level Water (LLW)

Analyze an aliquot of reagent water according to the procedure described in Section 3.4.

5.1.2 Low Level Soil (LLS)

Analyze 5.0 mL of reagent water according to the procedure described in Section 3.4.

5.1.3 Medium Level Soil (MLS)

Analyze 4.9 mL of reagent water and 100 µL of methanol according to the procedure described in Section 3.4.

5.1.4 Evaluation Criteria

A method blank must not contain more than five times the reporting limit of the following common laboratory solvents: methylene chloride, acetone and 2-butanone.

Evaluate internal standard response and retention times and surrogate spike recoveries as described in Sections 3.6.3 and 3.6.4. These criteria must be met prior to proceeding with sample analysis.

5.2 Lab Control Standard (LCS)

Prepare and analyze a LLW/LLS LCS each day LLW or LLS samples are run. Extract and analyze a MLS LCS with each batch of up to 20 MLS samples extracted together.

- For the LLW/LLS LCS, spike an aliquot of reagent water with 10 µL of the matrix spiking solution, and perform VOA analysis.
- For MLS samples, spike 8 mL of methanol with 1 mL of MLS Matrix Spiking Solution and perform VOA analysis.

Recovery of at least 12 of the 13 LCS compounds the surrogate standard compounds must meet the must meet the limits listed in Table 3. If the recovery of 2 or more LCS compounds or 1 surrogate compound is unacceptable, troubleshoot the GC/MS system and/or standards and obtain acceptable LCS recovery before proceeding with analysis.

5.3 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

Prepare and analyze an MS/MSD with every twenty samples of similar matrix and concentration.

- For LLW and LLS samples, take two additional aliquots of the selected sample(s), spiked with 10 μL of the matrix spiking solution, and perform VOA analysis.
- For MLS samples, take two additional aliquots spiked with 8 mL of methanol and 1 mL of MLS Matrix Spiking Solution and perform VOA analysis.
- When a sample requiring dilution has been chosen as the MS/MSD, the MS/MSD must be analyzed at the same dilution as the unspiked sample.

Calculate percent recovery as follows:

$$\text{Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Calculate the relative % difference (RPD) as follows:

$$RPD = \frac{2(D_1 - D_2)}{(D_1 + D_2)} \times 100$$

where D_1 = MS Result
D_2 = MSD Result

Advisory MS/MSD percent recovery and RPD limits are listed on Table 3. Since these limits are for advisory purposes only, they are not used to determine if sample reanalysis is required.

5.4 METHOD DETECTION LIMIT STUDIES

A method detection limit (MDL) study is performed annually according to 40 CFR 136, Appendix B. Statistically-based MDLs must be less than or equal to the reporting limit.

5.5 CONTROL LIMITS

The statistically-based limits for precision and accuracy listed in Table 3 are updated periodically and, therefore, subject to change.

6.0 INTERFERENCES

6.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method blanks. Use TFE-tubing and TFE-thread sealants. Avoid using flow controllers with rubber components in the purging device.

6.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal during storage and handling.

6.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross-contamination.

6.4 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to flush the purging device with a detergent solution, rinse it with distilled water, and dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; frequent bakeout and purging of the entire system may be required.

7.0 SAFETY PRECAUTIONS

7.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

7.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.2 Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDS).

7.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.4 Handle all glass equipment with care, particularly during assembly and disassembly.

7.5 Avoid contact with hot GC parts (e.g., injection ports or transfer lines).

7.6 Vent GC/MS mechanical pump exhaust to the outside.

8.0 APPARATUS AND MATERIALS

8.1 Micro syringes: 5-μL and larger, 0.006 inch ID needle.

8.2 Syringe valve: Two-way valve with Luer-lock ends (3-inch), if applicable to the purging device.

8.3 Syringe: 5.0-mL, gas tight with shut-off valve.

8.4 Balance:

8.4.1 **Analytical:** Capable of weighing to 0.0001 g.

8.4.2 **Top loading:** Capable of weighing to 0.1 g.

8.5 VOA vials: 40-mL, screw cap with teflon liner.

8.6 Flasks: Class A, volumetric with ground glass stoppers.

8.7 GC column: 105 m x 0.53 mm ID Rtx Volatiles or 60 m x 0.53 mm ID Rtx 502.2, or equivalent.

8.8 Purge and trap device: TEKMAR/LSC-2, Tekmar Model 4000/ALS or equivalent.

8.9 Gas Chromatograph/Mass Spectrometer (GC/MS): Finnigan 4023/9610, Finnigan Incos 50B or equivalent.

8.10 GC/MS Data System: Finnigan MAT-1 Incos or equivalent. System equipped with Super Incos software.

8.11 Autosampler: Dynatech PTA 30W or PTA 30W/S or equivalent. Calibrate the sample loop of each unit following installation.

8.12 Autosampler Vials: 16-mL capacity glass, screwtop vial with teflon-lined septum caps.

8.13 Dynatech Autosampler Soil Vial: 30-mL (approx.) capacity with fritted glass.

8.14 Vials: 2-mL glass with Teflon-sealed screw caps.

8.15 Volumetric Flasks: 5-mL and 10-mL capacity with ground glass stoppers.

9.0 REAGENTS

9.1 Reagent water: Deionized water passed through an activated carbon column.

9.2 Sodium thiosulfate: Granular, ACS grade.

9.3 Methanol: Pesticide quality or equivalent.

9.4 Stock standard solutions: Prepare from pure standard materials or purchase commercially; prepare stock standard solutions in methanol using assayed liquids or gases as appropriate.

9.5 Calibration Standards: Prepare calibration standards for each priority pollutant and TCL compound at five concentration levels from stock solutions: 20, 50, 100, 150, and 200 µg/L. Alternatively, varying amounts of a TCL composite standard may be used to obtain each of these concentrations.

9.6 Surrogate, Internal and Matrix Spiking Standard Solutions: Prepare the indicated solutions as follows:

9.6.1 **Medium Level Soil (MLS) Surrogate Spiking Solution** - Prepare a solution containing the following compounds in methanol.

Toluene-d_8	25 µg/mL
4-Bromofluorobenzene	25 µg/mL
1,2-Dichloroethane-d_4	25 µg/mL

9.6.2 **MLS Internal Standard Spiking Solution** - Prepare a solution containing the following compounds in methanol.

Bromochloromethane	50 µg/mL
1,4-Difluorobenzene	50 µg/mL

Chlorobenzene-d_5	50 μg/mL

9.6.3 **LLW/LLS Surrogate/Internal Standard Spiking Solution** - Prepare solutions containing surrogate and internal standards at a concentration of 125 and 250 μg/mL of each compound in methanol.

9.6.4 **4-Bromofluorobenzene (BFB) Standard** - Prepare a 50 μg/mL solution of BFB in methanol.

9.6.5 **LCS/Matrix Spiking Solution** - Prepare a solution containing the following compounds in methanol.

Benzene	25 ug/L
Chlorobenzene	25 ug/L
Chloroform	25 ug/L
Chloromethane	25 ug/L
1,1-Dichloroethane	25 μg/L
1,1-Dichloroethene	25 ug/L
1,2-Dichloropropane	25 ug/L
Ethylbenzene	25 ug/L
Methylbenzene [toluene]	25 ug/L
1,1,2,2-Tetrachloroethane	25 ug/L
Trichloroethene	25 μg/L
Tribromomethane [bromoform]	25 ug/L
Vinyl Chloride	25 ug/L

10.0 REFERENCES

10.1 U.S. EPA SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Volume IB, 1986, Method 8240 and Volume IB, 1992, Method 8260.

10.2 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984, Method 624.

10.3 U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM01.8.

TABLE 1

Volatile Organics Reporting Limits for TCL and Priority Pollutant Analyses[1]

Parameter	LLW/ LLS	MLS
chloromethane	10	1200
bromomethane	10	1200
vinyl chloride	10	1200
chloroethane	10	1200
methylene chloride	5	620
acetone	10	1200
carbon disulfde	5	620
1,1-dichloroethene	5	620
1,1-dichloroethane	5	620
1,2-dichloroethene (total)	5	620
trans-1,2-dichloroethane	5	620
chloroform	5	620
1,2-dichloroethane	5	620
2-butanone	10	1200
1,1,1-trichloroethane	5	620
carbon tetrachloride	5	620
bromodichloromethane	5	620
1,2-dichloropropane	5	620
cis-1,3-dichloropropene	5	620
trichloroethene	5	620
dibromochloromethane	5	620
1,1,2-trichloroethane	5	620
benzene	5	620
1,3-dichloropropene	5	620
trans-1,3-dichloropropene	5	620
2-chloroethylvinyl ether	5	620
bromoform	5	620
4-methyl-2-pentanone	10	1200
2-hexanone	10	1200
tetrachloroethene	5	620
toluene	5	620
1,1,2,2-tetrachloroethane	5	620
chlorobenzene	5	620
ethylbenzene	5	620
styrene	5	620
xylenes (total)	5	620

[1] LLW expressed as ug/L
LLS expressed as ug/Kg
MLS expressed as ug/Kg

TABLE 2

Internal Standard Assignments

Bromochloromethane:	1,4-Difluorobenzene:	Chlorobenzene:
1,2-dichloroethane-d4	vinyl acetate	4-methyl-2-pentanone
chloromethane	1,1,1-trichloroethane	toluene
vinyl chloride	carbon tetrachloride	tetrachloroethene
bromomethane	benzene	2-hexanone
chloroethane	trichloroethene	chlorobenzene
1,1-dichloroethene	1,2-dichloropropane	ethylbenzene
acetone	bromodichloromethane	xylenes
carbon disulfide	2-chloroethylvinyl ether	styrene
methylene chloride	cis-1,3-dichloropropene	1,1,2,2-tetrachloroethane
trans-1,2-dichloroethene	trans-1,3-dichloropropene	
1,1-dichloroethane	1,1,2-trichloroethane	
2-butanone	dibromochloromethane	
chloroform	bromoform	
acrolein		
acrylonitriletrichlorofluoromethane		
dichlorodifluoromethane		
cis-1,2-dichloroethene		

TABLE 3

GC/MS VOA Control Limits

QUALITY CONTROL TEST FILE
VOLATILE ORGANICS - GC/MS
WATER
PM: 00; AM: 020W

COMPOUND	COMBO	PRECISION AS RPD					PERCENT RECOVERY OF LAB CONTROL STANDARDS					PERCENT RECOVERY OF MATRIX SPIKES			
		WL	CL	X	S	CPK[1]	WL	CL	X	S	CPK[2]	95% CI	99% CI	X	S
1,1,1-trichloroethane	0850	≤12.3	≤16.2	4.40	3.93		79.9-111	72.0-119	95.66	7.88		79.6-116	70.5-126	98.01	9.18
1,1,2,2-tetrachloroethane	0C01	≤13.5	≤17.9	4.72	4.39		75.0-114	65.2-124	94.79	9.87		82.4-113	74.7-121	97.70	7.67
1,1,2-trichloroethane	0C03	≤11.6	≤15.4	4.21	3.72		83.4-115	75.5-123	99.04	7.84		84.7-114	77.3-122	99.56	7.43
1,1-dichloroethane	0C04	≤9.06	≤11.5	4.22	2.42		81.4-118	72.2-127	99.76	9.18		85.0-116	77.2-124	100.71	7.83
1,1-dichloroethene	0C05	≤11.3	≤14.9	4.18	3.58		67.4-129	52.1-144	97.95	15.29		59.3-131	41.5-149	95.04	17.86
1,2-dichloroethane	0C14	≤9.28	≤12.1	3.64	2.82		75.8-119	65.1-129	97.29	10.73		83.3-118	74.6-127	100.62	8.68
1,2-dichloropropane	0C16	≤10.1	≤13.3	3.89	3.13		77.1-115	67.6-124	96.00	9.45		86.2-114	79.3-121	99.93	6.87
2-butanone (MEK)	0C29	≤46.3	≤62.6	13.67	16.3		57.8-129	40.0-147	93.49	17.82		-	-	-	-
2-chloroethylvinyl ether	0C31	≤10.9	≤14.6	3.44	3.71		53.9-124	36.3-142	89.18	17.62[3]		51.9-133	31.6-153	92.43	20.26
2-hexanone	0C32	≤17.8	≤23.6	6.23	5.80		60.3-119	45.6-134	89.78	14.73		-	-	-	-
4-methyl-2-pentanone (MIBK)	0C38	≤14.3	≤19.2	4.51	4.91		62.8-125	47.1-141	94.11	15.68		-	-	-	-
acetone	0C40	≤30.9	≤40.7	11.29	9.80		56.5-136	36.5-156	96.32	19.93		-	-	-	-
benzene	0C44	≤9.22	≤12.1	3.42	2.90		79.4-111	71.5-119	95.07	7.85		80.4-122	70.0-133	101.28	10.42
bromodichloromethane	0C46	≤9.50	≤12.5	3.43	3.04		80.3-114	71.9-122	97.00	8.37		91.2-108	87.0-112	99.71	4.25
bromomethane	0C47	≤14.4	≤18.5	6.25	4.07		67.2-136	50.1-153	101.57	17.16		76.2-124	64.2-136	100.01	11.93
carbon disulfide	0C48	≤20.2	≤26.2	8.10	6.03		48.8-135	27.3-156	91.67	21.45		-	-	-	-
carbon tetrachloride	0C49	≤12.1	≤15.8	4.65	3.72		74.5-114	64.6-124	94.47	9.97		70.4-115	59.4-126	92.48	11.02
chlorobenzene	0C50	≤8.92	≤11.9	3.04	2.92		83.3-112	76.2-119	97.48	7.10		78.2-126	66.4-138	101.95	11.85
chloroethane	0001	≤15.5	≤19.9	6.71	4.39		66.6-130	50.7-146	98.35	15.88		69.6-122	56.4-136	95.98	13.21
chloroform	0002	≤8.07	≤10.5	3.14	2.46		78.7-119	68.6-129	98.86	10.07		69.3-130	54.2-145	99.53	15.12
chloromethane	0003	≤15.3	≤19.8	6.32	4.50		64.6-125	49.6-140	94.76	15.07		61.1-140	41.3-160	100.55	19.74
cis-1,3-dichloropropene	0005	≤10.1	≤13.4	3.72	3.21		78.1-110	70.2-117	93.83	7.86		84.2-110	77.8-116	96.94	6.39

TABLE 3
GC/MS VOA Control Limits (cont'd)
Page Two

QUALITY CONTROL TEST FILE
VOLATILE ORGANICS - GC/MS
WATER
PM: 00; AM: 020W

COMPOUND	COMBO	PRECISION AS RPD					PERCENT RECOVERY OF LAB CONTROL STANDARDS					PERCENT RECOVERY OF MATRIX SPIKES			
		WL	CL	X	S	CPK[1]	WL	CL	X	S	CPK[2]	95% CI	99% CI	X	S
dibromochloromethane	0008	≤10.5	≤13.9	3.84	3.32		82.1-115	73.9-123	98.41	8.16		81.1-117	72.1-126	99.20	9.03
dichloromethane [methylene chloride]	0013	≤16.2	≤21.4	5.69	5.25		79.2-117	69.8-127	98.18	9.47		83.4-127	72.6-137	104.98	10.80
ethylbenzene	0018	≤8.37	≤11.0	3.18	2.60		83.1-110	76.4-116	96.42	6.67		75.7-117	65.4-127	96.34	10.31
methylbenzene [toluene]	0032	≤11.5	≤15.5	3.59	3.96		79.4-112	71.2-121	95.94	8.25		76.6-118	66.2-128	97.27	10.36
styrene	0040	≤11.7	≤15.7	3.81	3.97		83.9-110	77.5-116	96.76	6.43		-	-	-	
tetrachloroethene	0041	≤10.8	≤14.3	3.80	3.50		64.2-123	49.5-138	93.65	14.71		44.7-136	21.8-159	90.50	22.91
trans-1,2-dichloroethene		≤9.90	≤12.9	3.89	3.01				98.29	8.46		-	-	-	-
trans-1,3-dichloropropene	0044	≤7.63	≤9.90	3.10	2.27		77.9-110	69.7-119	94.18	8.16		76.1-110	67.5-119	93.22	8.58
tribromomethane [bromoform]	0046	≤12.6	≤16.7	4.48	4.08		81.0-110	73.9-117	95.38	7.17		75.8-111	67.1-120	93.35	8.76
trichloroethene	0047	≤9.83	≤13.1	3.25	3.29		76.0-115	66.2-125	95.69	9.83		70.9-127	56.9-141	98.74	13.94
vinyl acetate	0E01	≤13.5	≤17.7	5.02	4.23		60.3-125	44.1-142	92.84	16.26		-	-	-	-
vinyl chloride	0E02	≤19.6	≤25.2	8.55	5.55		69.7-125	55.8-139	97.56	13.91		34.5-140	8.16-166	87.18	26.34
xylenes, total	0E03	≤10.8	≤14.2	3.78	3.49		82.5-112	75.2-119	97.17	7.33		-	-	-	-
1,2-dichloroethane-d4 (S)	0C15	NA	NA	NA	NA	NA	83.0-114	75.2-122	98.68	7.83		NA	NA	NA	NA
4-bromofluorobenzene (S)	0C37	NA	NA	NA	NA	NA	91.6-108	87.4-112	99.93	4.18		NA	NA	NA	NA
toluene-d8 (S)	0042	NA	NA	NA	NA	NA	91.2-113	85.8-118	101.89	5.37		NA	NA	NA	NA

TABLE 3
GC/MS VOA Control Limits (cont'd)
Page Three

QUALITY CONTROL TEST FILE
VOLATILE ORGANICS - GC/MS
SOIL
PM: 00; AM: 020SLL

COMPOUND	COMBO	PRECISION AS RPD					PERCENT RECOVERY OF LAB CONTROL STANDARDS					PERCENT RECOVERY OF MATRIX SPIKES			
		WL	CL	X	S	CPK[1]	WL	CL	X	S	CPK[2]	95% CI	99% CI	X	S
1,1,1-trichloroethane	OA02	-	≤40.0[6]	-	-	-	83.71-127	73.0-137	105.15	10.72	-	-	-	-	-
1,1,2,2-tetrachloroethane	OA03	-	≤40.0[6]	-	-	-	84.7-116	76.9-124	100.26[6]	7.79[6]	-	-	-	-	-
1,1,2-trichloroethane	OA04	-	≤40.0[6]	-	-	-	85.6-118	77.5-126	101.95[6]	8.15[6]	-	-	-	-	-
1,1-dichloroethane	OA05	-	≤40.0[6]	-	-	-	81.5-131	69.0-144	106.42[6]	12.47[6]	-	-	-	-	-
1,1-dichloroethene	OA06	≤30.5	≤40.8	10.06	10.24	-	68.7-138	51.2-156	103.62	17.46	-	46.6-141	23.0-164	93.75	23.57
1,2-dichloroethane	OA12	-	≤40.0[6]	-	-	-	85.3-133	73.5-145	109.05[6]	11.86[6]	-	-	-	-	-
1,2-dichloropropane	OA15	-	≤40.0[6]	-	-	-	85.7-122	76.6-131	103.89[6]	9.12[6]	-	-	-	-	-
2-butanone (MEK)	OA23	-	≤40.0[6]	-	-	-	17.5-164	-19.1-201	90.89[6]	36.68[6]	-	-	-	-	-
2-chloroethylvinyl ether	OA25	-	≤40.0[6]	-	-	-	-11.0-175	-57.6-222	82.00[3]	46.52[3]	-	-	-	-	-
2-hexanone	OA26	-	≤40.0[6]	-	-	-	15.5-154	-19.2-189	84.89[6]	34.69[6]	-	-	-	-	-
4-methyl-2-pentanone (MIBK)	OA31	-	≤40.0[6]	-	-	-	47.2-139	24.2-162	93.05[6]	22.95[6]	-	-	-	-	-
acetone	OA32	-	≤40.0[6]	-	-	-	24.8-126	-0.7-152	75.58[6]	25.41[6]	-	-	-	-	-
benzene	OA36	≤18.3	≤24.4	6.32	6.01	-	85.8-120	77.2-129	103.01	8.61	-	45.3-150	19.2-176	97.64	26.16
bromodichloromethane	OA38	-	≤40.0[6]	-	-	-	89.0-122	80.8-131	105.65[6]	8.29[6]	-	-	-	-	-
bromomethane	OA39	-	≤40.0[6]	-	-	-	76.9-134	62.6-148	105.37[6]	14.26[6]	-	-	-	-	-
carbon disulfide	OA40	-	≤40.0[6]	-	-	-	50.6-168	21.3-197	109.18[6]	29.28[6]	-	-	-	-	-
carbon tetrachloride	OA41	-	≤40.0[6]	-	-	-	82.8-125	72.3-135	103.84[6]	10.50[6]	-	-	-	-	-
chlorobenzene	OA42	≤17.1	≤22.6	6.02	5.54	-	89.0-113	83.0-119	100.81	5.93	-	42.3-133	19.6-155	87.54	22.63
chloroethane	OA43	-	≤40.0[6]	-	-	-	73.2-137	57.4-153	105.00[6]	15.88[6]	-	-	-	-	-
chloroform	OA44	-	≤40.0[6]	-	-	-	85.5-131	74.2-142	108.05[6]	11.27[6]	-	-	-	-	-
chloromethane	OA45	-	≤40.0[6]	-	-	-	61.0-155	37.6-178	107.90[3]	23.46[3]	-	-	-	-	-
cis-1,3-dichloropropene	OA47	-	≤40.0[6]	-	-	-	40.3-168	8.30-200	104.38[3]	32.03[3]	-	-	-	-	-

TABLE 3
GC/MS VOA Control Limits (cont'd)
Page Four

QUALITY CONTROL TEST FILE
VOLATILE ORGANICS - GC/MS
SOIL
PM: 00; AM: 020SLL

COMPOUND	COMBO	PRECISION AS RPD					PERCENT RECOVERY OF LAB CONTROL STANDARDS					PERCENT RECOVERY OF MATRIX SPIKES			
		WL	CL	X	S	CPK[1]	WL	CL	X	S	CPK[2]	95% CI	99% CI	X	S
dibromochloromethane	0A50	-	≤40.0[6]	-	-	-	82.0-127	70.6-139	104.7[3]	11.36[3]	-	-	-	-	-
dichloromethane (methylene chloride)	0803	-	≤40.0[6]	-	-	-	68.8-131	53.3-147	99.95[6]	15.56[6]	-	-	-	-	-
ethylbenzene	0808	-	≤40.0[6]	-	-	-	86.2-112	79.8-118	99.11[6]	6.43[6]	-	-	-	-	-
methylbenzene(toluene)	0821	≤19.6	≤26.0	6.90	6.37	-	85.5-114	78.3-122	99.93	7.20	-	38.5-145	11.9-171	91.71	59
styrene	0834	-	≤40.0[6]	-	-	-	84.9-113	77.9-120	98.84[6]	6.97[6]	-	-	-	-	-
tetrachloroethene	0836	-	≤40.0[6]	-	-	-	69.2-133	53.9-149	101.37[6]	15.82[6]	-	-	-	-	-
trans-1,2-dichloroethene	0839	-	≤40.0[6]	-	-	-	71.6-150	52.4-170	110.8[3]	19.59[3]	-	-	-	-	-
trans-1,3-dichloropropene	0840	-	≤40.0[6]	-	-	-	80.4-118	71.1-127	98.95[6]	9.28[6]	-	-	-	-	-
tribromomethane(bromoform)	0842	-	≤40.0[6]	-	-	-	83.1-119	74.0-129	101.26[6]	9.10[6]	-	-	-	-	-
trichloroethene	0843	≤17.1	≤22.5	6.26	5.42	-	85.0-116	77.2-124	100.62	7.82	-	46.5-127	26.4-147	86.78	20.12
vinyl acetate	0846	-	≤40.0[6]	-	-	-	48.1-129	27.7-150	88.72[6]	20.33[6]	-	-	-	-	-
vinyl chloride	0847	-	≤40.0[6]	-	-	-	60.1-141	39.8-162	100.74[6]	20.31[6]	-	-	-	-	-
xylenes, total	0848	-	≤40.0[6]	-	-	-	86.3-115	79.3-122	100.42[6]	7.05[6]	-	-	-	-	-
1,2-dichloroethane-d4 (S)	0A13	NA	NA	NA	NA	NA	75.7-115	66.0-124	95.15	9.71	-	NA	NA	NA	NA
4-bromofluorobenzene (S)	0A30	NA	NA	NA	NA	NA	78.2-117	68.6-126	97.48	9.62	-	NA	NA	NA	NA
toluene-d8 (S)	0838	NA	NA	NA	NA	NA	84.4-117	76.3-125	100.62	8.12	-	NA	NA	NA	NA

FIGURE 1

GCMS Assignment Sheet (29-Jul-92 Samples 206415 - 206416)

Due Date: ___-___-___ Date entered and init.: ___-___-___ _____
Approved and init.: ___-___-___ _____

Sample: P206416 Test: OVPPV Type: ORIG Run File Dilution Log Page Anlst/Processor(Empl#)
Analysis Number: 2 Anls. Ref. Number:
Analyst (Empl#) Number: _____
Date Analyzed: ___-___-___ Time: _____
Instrument: GCMS _____
Book: _____-_____ Page: _____
Sample Description: S/G MAUSOLEUM BUMP / ZNE EXT Time Sampled: Received Original (vol/wt): _____
Client: 17-JUL-92 Final (vol): _____
UNITS: _____ BLANK SAMPLE #: _____ RUN BATCH #: _____ Prep Meth: 00 Anls Meth: 0ZOME-
CASE ID: Not Available SDG: Not Available

VOLATILES

ANALYTE	DETECTION LIMIT	RESULT	QUALIFIER
1,1,1-Trichloroethane			
1,1,2,2-Tetrachloroethane			
1,1,2-Trichloroethane			
1,1-Dichloroethene			
1,1-Dichloroethane			
1,2-Dichloroethane			
1,2-Dichloroethene (total)			
1,2-Dichloropropane			
2-Chloroethylvinylether			
Acrolein			
Acrylonitrile			
Benzene			
Bromoform			
Bromomethane			
Carbon tetrachloride			
Chlorobenzene			
Chlorodibromomethane			
Chloroethane			
Chloroform			
Chloromethane			
Dichlorobromomethane			
Ethylbenzene			
Methylene chloride			
Tetrachloroethene			
Toluene			
Trichloroethene			
Vinyl chloride			
cis-1,3-Dichloropropene			
trans-1,3-Dichloropropene			

EXAMPLE ONLY

SURROGATES			
1,2-Dichloroethane-d4			
4-Bromofluorobenzene			
Toluene-d8			

COMMENTS: _____

Special Instructions

P206416 TYPE C

FIGURE 2

Halliburton NUS Laboratory Services Group--Pittsburgh

VOLATILE ORGANIC GC/MS ANALYSIS Notebook #:

Date:

Level: Low /Medium Matrix: Water /Soil /Other

Client:

PARAMETERS		STANDARDS:
Column:	He flow:	bfb:
Prog:	Col. head pressure:	is/su:
Source temp:	(inj. #):	hsl:
Trans. temp:	Cylinder Pressures:	gas:
Inj. temp:	He carrier:	extras:
Sep. temp:	air/N2:	
Initial Cali:	He purge:	
	Trap #:	Temp. tape:

Run#	File name	Ident	Dilution	Libr	Comments	Perm Tape

EXAMPLE ONLY

Comments:

Analyst :

Date:

Reviewer:

Date:

FIGURE 3

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Halliburton NUS
CORPORATION

NUS LABORATORY
5350 Campbells Run Road
Pittsburgh, Pennsylvania 15205

TEL: (412) 747-2500
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LABORATORY METHOD

BASE-NEUTRAL/ACID EXTRACTABLE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

METHOD ID: CRA/SN-BNA
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

BASE-NEUTRAL/ACID EXTRACTABLE ORGANICS ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

This method covers the determination of priority pollutant and US EPA CLP target compound list (TCL) semivolatile organics (base/neutral and acid extractables) in water and sediment/soil. Reporting limits for TCL and priority pollutant analyses are listed on Table 1; reporting limits for residential well analyses are listed in Table 2.

2.0 SUMMARY OF METHOD

Water samples are prepared for analysis by liquid-liquid solvent extraction at pH >11 and pH <2. Procedures for continuous and separatory funnel extractions are provided. Soil/sediment samples are prepared for analysis by sonication. A low level extraction using 30 grams of sample is used routinely. However, for samples containing more than 20 mg/kg semivolatile and nonvolatile organics, a medium level extraction procedure using 1 gram of sample is used.

Semivolatile compounds in the extract are transferred from the liquid phase to the vapor phase by injecting a portion of the combined BNA extract into a heated capillary GC column injection port in the "splitless" mode. The semivolatile compounds are swept onto a fused silica capillary gas chromatographic column by the inert carrier gas (He). The gas chromatograph is temperature-programmed to separate the semivolatile compounds, which are then detected with a mass spectrometer operating in the electron ionization (EI) mode.

Approvals:

Technical Operations Manager	Date 4/12/94	Quality Assurance Director	Date 4/12/94	Group Leader	Date 4/

3.0 EXTRACTION PROCEDURES

3.1 SAMPLE PRESERVATION

3.1.1 Water Samples

Water samples are stored at 1 - 5 degrees C. Extraction must be completed within 7 days of sampling.

3.1.2 Soil/Sediment Samples

Soil/sediment samples are stored at 1 - 5 degrees C. Extraction must be completed within 14 days of sampling.

3.2 CONTINUOUS LIQUID-LIQUID EXTRACTION OF AQUEOUS SAMPLES

3.2.1 Set up the extraction equipment in an operating fume hood.

3.2.2 Close the extractor body stopcock.

3.2.3 Add approximately 300 mL of methylene chloride measured in a 500-mL graduated cylinder to the extractor body. Add approximately 300 mL of methylene chloride and several boiling chips to a 1000-mL round-bottom flask.

3.2.4 Shake the sample container to mix the contents thoroughly. Measure 1 liter of sample in a glass 1-liter graduated cylinder.

3.2.5 Check the pH of the sample with wide-range pH paper as follows:

3.2.5.1 Stir the sample with a glass rod to thoroughly mix the contents.

3.2.5.2 Quickly touch the end of the glass rod to a strip of wide-range pH paper. Check the colorimetric result to determine the pH of the sample.

3.2.5.3 Adjust the pH >11 as follows:

- Make pH adjustments with 10N NaOH to raise the pH. Add a small amount (approx. 1 mL) of the or NaOH using a Pasteur pipet.
- Stir the contents to mix thoroughly and recheck the pH.
- Repeat the addition of NaOH as necessary to adjust the sample to the desired pH.

3.2.6 Transfer the 1 liter sample to the extractor body.

3.2.7 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of the surrogate standard spiking solution into each sample in the extractor and mix well.
- Prepare a lab control standard (LCS) by spiking the indicated volume of the LCS/matrix spiking solution into 1 liter of reagent water with each batch of samples extracted.
- For samples selected for matrix spiking, add the indicated volume of the matrix spiking standard and mix well.

3.2.8 Assemble the extraction equipment as follows:

3.2.8.1 Insert the condenser into the top of the extractor body.

3.2.8.2 Maintain the extractor body in an upright position using a large clamp attached to a ring stand or similar support.

3.2.8.3 Attach the round-bottom flask to the side-arm of the extractor body.

3.2.8.4 Place the round-bottom flask in a heating mantle.

3.2.8.5 Use Teflon tape to seal all the joints.

3.2.9 Extract the sample as follows:

3.2.9.1 Open the extractor body stopcock.

3.2.9.2 Turn on the water supply to the condenser.

The water pressure should be sufficient to cycle the water in the condenser, but should not force off any tubing connections from the water supply to the condenser.

3.2.9.3 Turn on the heating mantle and adjust the temperature setting to "7".

3.2.9.4 Extract the sample for 18-24 hours.

3.2.9.5 Check the extractor body/condenser periodically during the extraction process for the following:

- A drip rate of approximately 1-2 drops/second from the bottom of the condenser into the extractor body.
- Approximately 1/4 to 1/3 of the bottom of the condenser should be wet from the extract if the distillation is proceeding at the proper temperature.

Adjust the heating mantle temperature setting as necessary to achieve these conditions.

3.2.10 Turn off the power to the heating mantle when the extraction is complete. Allow the flask to cool for approximately 1.5 hours before removing it from the extractor body.

3.2.11 Save the base/neutral extract for combining with the acid extract prior to concentration. Store the base/neutral extract in the dark (to prevent photodegradation) in a tightly stoppered container at room temperature during the acid extraction procedure.

3.2.12 Adjust the pH of the aqueous phase to <2 with sulfuric acid (1:1) as follows. Do not overacidify.

3.2.12.1 Add a small amount (approx. 1 mL) of H_2SO_4 (1:1) to the extractor body using a Pasteur pipet. Stir the contents to mix thoroughly.

3.2.12.2 Quickly dip the end of a clean glass rod into the contents and touch it to a strip of wide-range pH paper. Check the colorimetric result to determine the pH of the sample.

3.2.12.3 Repeat the addition of H_2SO_4 and recheck the pH as necessary to adjust the pH to <2.

3.2.13 Attach a clean round-bottom flask containing approximately 500 mL of methylene chloride to the extractor body. Use Teflon tape to seal the joint. Extract as described before in steps 3.2.9 and 3.2.10.

3.2.14 Combine the acid and base/neutral extracts by pouring the base/neutral extract into the flask containing the acid extract. Rinse the base/neutral extract flask with 20-30 mL of methylene chloride to complete the transfer.

3.2.15 Prepare a drying column containing anhydrous sodium sulfate. See Section 9.1.2 for instructions on column preparation. Set up the drying column using a clamp attached to a ring stand.

Connect a 500-mL Kurderna-Danish (K-D) evaporation flask to a 10-mL concentrator tube. Place the K-D apparatus beneath the column to collect the extract.

3.2.16 Close the extractor body stopcock. Remove the flask containing the solvent extract and carefully pour the extract through the column. Collect the dried extract in the K-D apparatus. If the sodium sulfate hardens at any point during the drying process:

3.2.16.1 Break up the hardened mass, if possible, with a pipet and add 20-30 mL of elution solvent to the column to rinse it.

3.2.16.2 Start a new drying column, if necessary, to pass through any remaining solvent extract.

3.2.16.3 Repeat these steps as necessary until all the solvent fractions have been passed through drying columns into the collection device.

3.2.17 Concentrate the extract as follows:

3.2.17.1 Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

3.2.17.2 Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

3.2.17.3 Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

3.2.17.4 Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

3.2.17.5 Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.2.18 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of 1:1 (v:v) methylene chloride:acetone.

3.2.19 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.3 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION OF AQUEOUS SAMPLES

3.3.1 Set up the extraction equipment in an operating fume hood. Put the separatory funnel, with the Teflon stopcock closed, into a large metal ring attached to a ring stand.

3.3.2 Shake the sample container to mix the contents thoroughly. Measure 1 liter of sample in a glass graduated cylinder and transfer it quickly to the separatory funnel. Stopper the funnel.

3.3.3 Check the pH of the sample with wide-range pH paper as follows:

3.3.3.1 Invert the funnel, open the stopcock and swirl to mix the contents. Close the stopcock, replace the funnel in the ring stand and remove the stopper.

3.3.3.2 Quickly dip the end of a clean glass rod into the funnel contents and touch it to a strip of wide-range pH paper. Check the colorimetric result to determine the pH of the sample.

3.3.3.3 Adjust the pH to >11 as follows:

- Adjust the pH using 10N NaOH to raise the pH. Add a small amount (approx. 1 mL) of the NaOH using a Pasteur pipet.
- Stopper the funnel, swirl the contents to mix thoroughly and recheck the pH.
- Repeat the addition of NaOH as necessary to adjust the sample to the desired pH.

3.3.4 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of the surrogate standard spiking solution into each sample in the funnel and mix well.
- Prepare a lab control standard (LCS) by spiking the indicated volume of the LCS/matrix spiking solution into 1 liter of reagent water with each batch of samples extracted.
- For samples selected for matrix spiking add the indicated volume of the matrix spiking standard and mix well.

3.3.5 Add approximately 60 mL of methylene chloride measured in a 100-mL graduated cylinder to the separatory funnel.

3.3.6 Seal the separatory funnel. Invert once and vent the funnel into the hood by opening the stopcock. While the stopcock is still open, swirl the contents of the flask to mix well.

Note: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted once.

Close the stopcock. Shake the inverted funnel vigorously for 1-2 min. with periodic venting through the stopcock to release excess pressure.

3.3.7 Replace the funnel in the ring stand. Allow the organic layer to separate from the water phase for a minimum of 10 minutes.

If the emulsion interface between layers is more than one-third the size of the solvent layer, use mechanical techniques to complete the phase separation. The best technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Consult with the Group Leader, if required, to determine the best method for optimum separation. Document such measures in the extraction log.

3.3.8 Prepare a drying column containing anhydrous sodium sulfate. See Section 9.1.2 for instructions on column preparation. Set up the drying column near the separatory funnel using a clamp attached to the ring stand.

Place the initial base/neutral extract in a 250-mL Erlenmyer flask and the acid extract directly into a K-D apparatus.

3.3.9 Hold the separatory funnel over the drying column and open the stopcock to remove the solvent fraction. Dry the extract by passing it through the drying column. Collect the dried extract in a 250-mL Erlynmeyer flask. If the sodium sulfate hardens at any point during the drying process:

3.3.9.1 Break up the hardened mass, if possible, with a pipet and add 20-30 mL of elution solvent to the column to rinse it.

3.3.9.2 Start a new drying column, if necessary, to pass through any remaining solvent extract.

3.3.9.3 Repeat these steps as necessary until all the solvent fractions have been passed through drying columns into the collection device.

3.3.10 Repeat the solvent extraction two more times using fresh portions of solvent (steps 3.3.5 through 3.3.9). Collect the three solvent extracts in the same collection device.

Add 20-30 mL of methylene chloride to the column to complete the quantitative transfer.

3.3.11 Save the base/neutral extract for combining with the acid extract prior to concentration. Store the base/neutral extract in a covered container (e.g., a foil covering over the flask opening) at room temperature during the acid extraction procedure.

3.3.12 Adjust the pH of the aqueous phase to <2 with sulfuric acid as follows. Do not overacidify.

3.3.12.1 Add a small amount (approx. 1 mL) of H_2SO_4 (1:1) to the funnel using a Pasteur pipet. Stopper the funnel and swirl the contents to mix thoroughly.

3.3.12.2 Quickly dip the end of a clean glass rod into the funnel contents and touch it to a strip of wide-range pH paper. Check the colorimetric result to determine the pH of the sample.

3.3.12.3 Repeat the addition of H_2SO_4 and recheck the pH as necessary to adjust the pH to <2.

3.3.13 Add approximately 60 mL of methylene chloride to the separatory funnel. Extract and dry as described before in steps 3.3.5 to 3.3.10.

3.3.14 Combine the acid and base/neutral extracts by pouring the base/neutral extract into the K-D apparatus containing the acid extract. Rinse the base/neutral extract flask with 20-30 mL of methylene chloride to complete the transfer.

3.3.15 Concentrate the extract as follows:

3.3.15.1 Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

3.3.15.2 Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

3.3.15.3 Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers <u>will not flood</u>.

3.3.15.4 Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

3.3.15.5 Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.3.16 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of 1:1 (v:v) methylene chloride:acetone.

3.3.17 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.4 SONICATION EXTRACTION OF IN SOIL/SEDIMENT

3.4.1 <u>Sample Preparation</u>

Decant and discard any water layer. Discard foreign objects such as sticks, vegetation, and rocks. Mix the sample thoroughly, especially composited samples.

3.4.2 Low Level Soil Extraction and Initial Concentration

3.4.2.1 Tune the sonicator as described in Table 4 to check its operation.

3.4.2.2 Aliquot the samples as follows. Perform these steps rapidly to avoid loss of the more volatile extractables:

a. Place a 400-mL glass beaker on the weighing pan of a balance and tare the balance.

b. Mix the sample thoroughly with a spatula and transfer approximately 30 grams of sample to the beaker. Record the weight to the nearest 0.01 gram.

c. Mix nonporous or wet samples (i.e., gummy or clay type samples) that do not have a free-flowing and/or sandy texture with anhydrous sodium sulfate to dry them as follows:

- Tare the balance holding the sample beaker.
- Add approximately 30 grams of anhydrous sodium sulfate to the beaker. Record the weight to the nearest 0.01 gram.
- Mix thoroughly using a spatula. Check if the texture appears free-flowing and/or sandy.
- Add additional anhydrous sodium sulfate in 30 gram increments (approx.) as necessary until the sample consistency is free-flowing and/or sandy.
- Record the total amount of sodium sulfate to the nearest 0.01 gram.

3.4.2.3 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of surrogate standard spiking solution onto each sample in the beaker.

- Prepare a lab control standard (LCS) by spiking the indicated volume of the LCS/matrix spiking solution onto 30 grams of clean sand with each batch of samples extracted.

- For samples selected for matrix spiking add the indicated volume of the matrix spiking standard.

3.4.2.4 Immediately add approximately 100 mL of 1:1 (v:v) methylene chloride:acetone measured in a glass graduated cylinder.

3.4.2.5 Sonicate the sample as follows:

a. Attach the ¾-inch disrupter horn (No. 207) to a heavy-duty ring stand using a large vinyl-coated clamp. See Section 9.1.17 for additional information on the equipment.

b. Place the tip of the disrupter horn about ½-inch below the surface of the solvent but above the sediment layer.

c. Sonicate for 3 minutes with the output control knob set at 8 to 10, the mode switch on "Pulse" and the percent-duty cycle knob set at 20%.

- The solvent layer should be "churning" but not overflowing the sides of the beaker.

- Do not touch the tip of the disrupter horn to the sides or bottom of the beaker because damage to the horn or beaker may occur.

3.4.2.6 Decant the extract through Whatman No. 41 filter paper lining a glass funnel. Collect the extract into a Kuderna-Danish (K-D) 10-mL concentrator tube attached beneath a 500-mL evaporation flask.

3.4.2.7 Repeat the sonication two more times with additional 100 mL portions of solvent. Decant and filter the solvent phase after each sonication.

On the final filtration, transfer the entire sample into the funnel. Rinse the beaker with approximately 20-30 mL of solvent to complete the quantitative transfer.

3.4.2.8 Concentrate the extract as follows:

a. Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

b. Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

c. Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

d. Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

e. Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.4.2.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of 1:1 (v:v) methylene chloride:acetone.

3.4.210 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.4.3 Medium Level Soil Extraction and Initial Concentration

3.4.3.1 Tune the sonicator as described in Table 4 to check its operation.

3.4.3.2 Aliquot the samples as follows. Perform these steps rapidly to avoid loss of the more volatile extractables:

a. Place a 10-mL glass scintillation vial on the weighing pan of a balance and tare the balance.

b. Mix the sample thoroughly with a spatula and transfer approximately 1 gram of sample to the vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the weight to the nearest 0.01 gram.

c. Mix nonporous or wet samples (i.e., gummy or clay type samples) that do not have a free-flowing and/or sandy texture with anhydrous sodium sulfate to dry them as follows:

- Tare the balance holding the sample vial.
- Add approximately 1 gram of anhydrous sodium sulfate to the vial. Record the weight to the nearest 0.01 gram.
- Mix thoroughly using a spatula. Check if the texture appears free-flowing and/or sandy.
- Add additional anhydrous sodium sulfate in 1 gram increments (approx.) as necessary until the sample consistency is free-flowing and/or sandy.
- Record the total amount of sodium sulfate to the nearest 0.01 gram.

3.4.3.3 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of surrogate standard spiking solution onto each sample in the vial.
- Prepare a lab control standard (LCS) by spiking the indicated volume of LCS/matrix spiking solution onto 1 gram of clean sand with each batch of samples extracted.
- For samples selected for matrix spiking add the indicated volume of matrix spiking standard.

3.4.3.4 Immediately add enough 1:1 (v:v) methylene chloride:acetone to bring the final volume to 10.0 mL including the surrogate and/or matrix spike volumes.

3.4.3.5 Sonicate the sample as follows:

a. Attach the 1/8-inch microtip ultrasonic probe (No. 419) to a heavy-duty ring stand using a large vinyl-coated clamp. See Section 9.1.17 for additional information on the equipment.

b. Place the tip of the probe below the surface of the solvent but above the sediment layer.

c. Sonicate for approximately 3 minutes with the output control knob set at 4 to 5, the mode switch on "Pulse" and the percent-duty cycle knob set at 20%.

- The solvent layer should be "churning" but not overflowing the sides of the vial.
- Do not touch the tip of the probe to the sides or bottom of the vial because damage to the horn or vial may occur.

3.4.3.6 Filter the extract as follows:

a. Loosely pack a Pasteur pipet with a small plug of clean glass wool. See Section 9.1.2 for detailed instructions on pipet preparation.

b. Using a small clamp attached to a ring stand, support the filtering pipet in an upright position over a Kuderna-Danish (K-D) 10-mL concentrator tube.

c. Use a separate pipet to transfer the extract from the vial to the filtration apparatus.

d. Collect the extract to the 5 mL mark of the concentrator tube by gravity filtration through the glass wool.

3.4.3.7 Concentrate the extract as follows:

a. Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

b. Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

c. Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

d. Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

e. Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.4.3.8 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of 1:1 (v:v) methylene chloride:acetone.

3.4.3.9 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.5 FINAL EXTRACT CONCENTRATION

Note: Final concentration of the extract is completed by the micro Snyder technique described below (step 3.6.1) or the nitrogen blowdown technique (step 3.6.2).

3.5.1 Concentrate the extract as follows:

3.5.1.1 Add one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of solvent to the top of the column.

3.5.1.2 Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Swirl the tube in the water if necessary to begin the distillation process.

3.5.1.3 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

3.5.1.4 When the apparent volume of liquid reaches approximately 0.5 mL, remove the K-D apparatus from the water bath. Allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

3.5.1.5 Remove the Snyder column. Adjust the final volume to 1.0 mL with methylene chloride.

3.5.2 An alternate procedure to step 3.5.1 is the nitrogen blowdown technique as described below:

3.5.2.1 Place the concentrator tube in the heating block set at 30-35°C. Evaporate the solvent to 0.5-0.8 mL using a gentle stream of clean, dry nitrogen gas dispensed through a Luer-Lock blunt tip needle.

Do not allow the extract to become dry. If this occurs, repeat the extraction.

Use a clean, dry Luer-Lock blunt tip needle for each sample.

3.5.2.2 Adjust the final volume to 1.0 mL with methylene chloride.

3.5.3 Transfer the extract to a Teflon-sealed, screw-cap vial labeled with the sample number, fraction, and extraction date.

4.0 GC/MS ANALYSIS

4.1 EXTRACT PRESERVATION

Store extracts at 1 - 5 degrees C. Complete analysis within 40 days of extraction.

4.2 PREPARATION OF STANDARDS

Stock standards are purchased commercially in sealed ampoules. Depending on the concentration of the purchased solution, intermediate or working standards are prepared in methylene chloride. Aliquots of stock solutions are combined as necessary to prepare intermediate or working standards that contain the analytes of interest. Prepare standard solutions as follows.

4.2.1 Check the expiration date on any stock or intermediate standard to be diluted. Discard material exceeding the expiration date according to waste management procedures.

4.2.2 Determine the appropriate volume of standard material to add to the flask to obtain the desired final concentration as follows:

$$V = (DC/SC) \times FV$$

where V = volume of standard material to be added
DC = desired concentration
SC = standard material concentration
FV = final volume

4.2.3 Fill a volumetric flask just to the neck with dilution solvent.

4.2.4 Using a syringe, quickly transfer the appropriate amount of standard to the flask to obtain the desired concentration in µg/mL. Use a syringe to add the liquid material directly to the solvent without contacting the neck of the flask. Immerse the needle tip below the surface of the solvent before expelling the solution to reduce evaporation of the standard material.

4.2.5 Add dilution solvent until the bottom of the meniscus reaches the volume mark of the flask using a disposable pipet. Place the tip of the pipet close to the volume mark without immersing it in the dilution solvent. Avoid wetting the neck of the flask above the volume mark.

4.2.6 Stopper the flask and invert three times to mix thoroughly.

4.2.7 Transfer aliquots of intermediate standard solutions to 2-mL vials without headspace using a Pasteur pipet. Label bottles or vials containing standard solutions with the following information:

- Solution name and concentration - use sufficient detail in the description to identify it from other solutions.
- Identification number.
- Date prepared and preparer.
- Expiration date.

4.2.8 Store volatile and semivolatile standard solutions in separate refrigerated storage areas to prevent cross-contamination of standard materials and/or solvents.

Store standard solutions in Teflon-sealed containers at $\leq$ 4° C. Use amber glass vials to protect semivolatile standard solutions from photodegradation.

Mark the meniscus level on any container where headspace in the vial is apparent.

4.2.9 Visually check standard stock solutions prior to use for evidence of degradation or evaporation. Replace the solutions every six months, or sooner if degradation or evaporation occurs or if comparison with quality control check samples indicate a problem.

4.3 INSTRUMENT SET-UP AND TUNING

4.3.1 Set the GC/MS operating conditions as follows:

Parameter	Operating Condition
Column Type	30 m x 0.32 mm ID bonded phase silicone coated fused silica capillary column with DB-5, or equivalent
Flow Rate/Gas	60 cm/sec/Helium
Column Temperature	Isothermal at 40°C for 1 minute, increase to 300°C at 10°C/minute, hold for 7 minutes
Electron Energy	70 volts (nominal)
Mass Range	35 to 500 daltons
Scan Time	1 second per scan or less
Injector Temperature	275°C
Separator Oven Temperature	300°C
Source Temperature	140°C

4.3.2 At the start of each 12.0-hour period of analysis, tune the instrument as follows:

4.3.2.1 Manually inject 50 ng of DFTPP and check that the GC/MS meets the standard mass spectral ion abundance criteria listed below:

Mass	DFTPP Ion/Abundance Criteria
51	30.0-60.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	mass 69 relative abundance
70	less than 2.0 percent of mass 69
127	40.0-60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0-9.0 percent of mass 198
275	10.0-30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present, but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0-23.0 percent of mass 442

4.3.2.2 If criteria are not met, retune the system. Do not proceed with analysis until a successful tune is performed.

4.3.2.3 Repeat the DFTPP calibration every 12 hours of operation or whenever corrective actions are taken that change or affect the tuning criteria (e.g., ion source cleaning or repair). The 12-hour period begins with the DFTPP injection.

4.4 INITIAL CALIBRATION

4.4.1 Prepare a 5-point initial calibration curve as follows:

4.4.1.1 Place 20 µL (approx.) of the 20, 50, 80, 120 and 160 µg/mL calibration standards into separate, 1-mL amber glass conical vials with crimp-top septum caps. Place in the autosampler tray and start the autosampler.

4.4.1.2 The autosampler withdraws 5 μL from the vial to pre-rinse the syringe. It then withdraws and injects 1.0 μL onto the GC column. The autosampler then rinses the syringe with ten 10-μL portions of methylene chloride.

4.4.2 Tabulate the area response of the characteristic ions against concentration for each compound and internal standard and calculate relative response factor (RF) for each compound using the following equation:

$$RRF = \frac{Ax}{Ais} \times \frac{Cis}{Cx}$$

where Ax = Area of the characteristic ion for the compound to be measured

Ais = Area of the characteristic ion for the specified internal standard (see Table 5)

Cis = Concentration of the internal standard

Cx = Concentration of compound to be measured

4.4.3 Calculate the average relative response factor (RRF_{ave}) for each compound. The RRF_{ave} of the System Performance Check Compounds (SPCC) listed below must be at least 0.050.

SPCC

N-Nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

4.4.4 Calculate the % relative standard deviation (% RSD) of RRF values for each compound as follows:

$$\% \text{ RSD} = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

The % RSD of the Calibration Check Compounds (CCC) listed below, must be $\leq$30.0%.

CCC

Acenaphthene	Phenol
1,4-Dichlorobenzene	2-Nitrophenol
Hexachlorobutadiene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	2,4,6-Trichlorophenol
Fluoranthene	Pentachlorophenol
Di-n-octyl phthalate	2,4-Dichlorophenol
Benzo(a)pyrene	

4.4.5 Once the criteria for initial calibration have been met, report the RRF_{ave} and % RSD for all compounds.

If the minimum response factors or the % RSD are not met, evaluate the system and take action to correct the problems prior to proceeding with sample analysis.

4.5 CONTINUING CALIBRATION

4.5.1 Analyze a 50 µg/mL calibration standard(s) containing all semi-volatile compounds every 12 hours immediately after a successful DFTPP tune.

4.5.2 Perform a system performance check as described in step 3.2.3. Calculate the relative response factor (RRF) for each compound. The RRF of the System Performance Check Compounds (SPCC) listed below must be at least 0.050.

SPCC

N-Nitroso-di-n-propylamine
Hexachlorocyclopentadiene
2,4-Dinitrophenol
4-Nitrophenol

If SPCC criteria are not met, take corrective actions to isolate and correct the problem.

4.5.3 Perform a continuing calibration check to verify the validity of the initial calibration by calculating the % difference of the RRF for each CCC as follows:

$$\% \text{ Difference} = \frac{RRF_{ave} - RRF_c}{RRF_{ave}} \times 100$$

where RRF_{ave} = average response factor from initial calibration.

RRF_c = response factor from current continuing calibration standard

The % difference of the Calibration Check Compounds (CCC) listed below, must be $\leq$25.0%.

CCC	
Acenaphthene	Phenol
1,4-Dichlorobenzene	2-Nitrophenol
Hexachlorobutadiene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	2,4,6-Trichlorophenol
Fluoranthene	Pentachlorophenol
Di-n-octyl phthalate	2,4-Dichlorophenol
Benzo(a)pyrene	

Proceed as indicated below after calculating the % difference:

4.5.3.1 If the % difference for each CCC is $\leq$ 25.0%, assume the initial calibration is valid and continue analysis.

4.5.3.2 If the % difference for any CCC is > 25.0%, take corrective action.

4.5.3.3 If the source of the problem cannot be determined, generate a new five-point initial calibration curve. The calibration criteria must be met before analysis can continue.

Note: If continuing calibration is being performed for a limited set of compounds (e.g., PAHs or TCLP semivolatiles), sample analysis may proceed as long as the response factor exceeds 0.300 and the % difference is $\leq$ 25.0% for each target analyte.

4.6 SAMPLE ANALYSIS

4.6.1 Transfer 100 µL of BNA extract into a 2-mL GC autosampler vial. Add 5.0 µL of internal standard spiking solution for a final concentration of 40 µg/mL for each internal standard compound.

4.6.2 The autosampler withdraws 5 µL from the vial to pre-rinse the syringe. It then withdraws and injects 1.0 µL of extract onto the GC column. The autosampler then rinses the syringe with ten 10-µL portions of methylene chloride.

4.6.3 If any compound in the sample exceeds the linear calibration range of the system, clean the GC/MS by analyzing solvent blanks, until a blank free of interferents is obtained. Reanalyze the sample at a dilution at which no target compound is saturated.

4.6.4 Tabulate the retention time and EICP area of each internal standard against the most recent 12-hour continuing calibration standard.

If the following criteria are not met, reanalyze the sample:

- The retention time for any internal standard must not change by more than 30 seconds from the latest 12-hour calibration standard.
- The extracted ion current profile (EICP) area for any internal standard must not change by more than a factor of two (-50% to +100%).

4.6.5 Calculate the surrogate spike recoveries as follows:

$$\text{Percent Surrogate Recovery} = \frac{Qd}{Qa} \times 100$$

where Qd = quantity determined by analysis
Qa = quantity added to sample

The surrogate spike recoveries must be within the limits listed on Table 6. If recovery of any surrogate is less than 10%, or more than one acid and one base-neutral fraction surrogate exceeds limits, the sample must be re-extracted and reanalyzed.

4.7 IDENTIFICATION OF TARGET COMPOUNDS

4.7.1 Identify semivolatile target compounds by comparison of the sample and standard mass spectra generated during a 12-hour period.

4.7.2 Positively identify a compound by meeting the following criteria:

- The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the standard component.
- All ions present in the standard mass spectrum at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
- The relative intensities of ions specified in the above paragraph must agree within ± 20% absolute intensity between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. When GC/MS computer

data enhancement programs are used to obtain the sample component spectrum, both the enhanced and the raw spectra must be evaluated. The verification process should favor false positives for BNA identifications.

4.8 QUANTITATION OF TARGET COMPOUNDS

4.8.1 Quantitate target components by the internal standard method. The internal standard nearest the retention time of a given analyte is used for quantitation (see Table 5).

4.8.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the response factor as determined in step 4.4.2 and the following equations:

4.8.2.1 Water samples

$$\text{Concentration (in } \mu\text{g/L)} = \frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where
- A_x = Area of the characteristic ion for the compound to be measured
- A_{is} = Area of the characteristic ion for the internal standard
- I_s = Amount of internal standard injected (ng)
- V_o = Volume of water extracted (mL)
- V_i = Volume of extract injected (μL)
- V_t = Volume of total extract (μL)

4.8.2.2 Sediment/soil samples

$$\text{Concentration (in } \mu\text{g/kg)} = \frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

where
- A_x, I_s, A_{is} = same as above for water samples
- V_t = Volume of low level total extract (Use 1000 μL or a factor of this when dilutions are made. The 1000 μL is derived from concentrating the 9.5 mL extract to 0.95 mL.)

OR

Volume of <u>medium level</u> extract (Use 2000 μL or a factor of this when dilutions are made. The 2000 μL is derived from concentrating 5 mL of the 10 mL extract to 1 mL.)

V_i = Volume of extract injected (μL)
W_s = Wet weight of sample extracted (gm)

5.0 DATA COLLECTION

5.1 EXTRACTION

Document the following in a bound lab notebook for each set of extractions performed. Entries must be made at the time of extraction and concentration. An example logbook entry is shown in Figure 1 and briefly described below:

- preparation method code (root code) and brief description (e.g., LLW BNAs).
- date and time extraction started and completed, and analyst(s) signature(s).
- date and time concentration started and completed, and analyst(s) signature(s).
- method of final concentration (water bath or nitrogen blowdown technique).
- lab sample number, sample aliquot, and descriptive codes (see Table 7) for each sample. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- Spikes added, to include the spiking solution identification number and the volume of spike added.

Forward the following to data management from each 12-hour tune for data package preparation:

- description of problems encountered and actions taken during sample analysis on corrective action records.
- logbook page(s).

5.2 ANALYSIS

Document all data in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. Examples of appropriate forms for data collection (i.e., assignment sheets and injection log) are shown on Figures 2-3.

Data collection should include the following:

- method code and brief description (e.g., GC/MS - Semivolatiles).
- instrument parameters.
- date and time of DFTPP injection, and analyst(s) signature(s).
- lab sample number and aliquot, and data system filename. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added.

Forward the following to data management from each 12-hour tune for data package preparation:

- description of problems encountered and actions taken during sample analysis on corrective action records.
- initial and continuing calibration files.
- tune files.
- sample and associated quality control sample files (method blank, lab control standard, MS/MSD).
- Chromatograms, quantitation reports, and mass spectra for samples and associated quality control samples.
- logbook page(s) and assignment sheets.

6.0 QUALITY CONTROL

6.1 SOLVENT PRESCREEN

Prescreen each lot of solvent prior to use as described in LSG Procedure AP-001, Reagent Screening Program. Use only approved lots of solvent in sample extraction.

6.2 METHOD BLANKS

Method blanks must be prepared and analyzed with each batch of up to twenty samples of similar concentration and matrix extracted together.

Analyze and evaluate the method blanks as described in Section 4.6 concurrently with the samples from the batch. Each blank must meet the following additional criteria:

- The method blank must not contain more than five times the reporting limit of any phthalate ester, and less than the reporting limit of all other target compounds.
- The surrogate spike recoveries of the method blank must be within the limits listed on Table 6. If they are not, take corrective measures before sample analysis proceeds, which may include verification of the spiking solution.

6.3 LAB CONTROL STANDARD (LCS)

An LCS must be prepared and analyzed with each batch of up to twenty samples of similar concentration and matrix extracted together.

Analyze and evaluate an LCS as described in Section 4.6 concurrenly with the samples from the batch. Each LCS must meet the following criteria: recovery of at least 17 of the 18 LCS compounds the surrogate standard compounds must meet the must meet the limits listed in Table 6. If the recovery of 2 or more LCS compounds is unacceptable, troubleshoot the GC/MS system, extraction, and/or standards. Re-extract the associated samples.

6.4 SURROGATE STANDARDS

Calculate surrogate spike recovery for each surrogate compound in each standard, sample, blank, matrix spike and matrix spike duplicate to monitor both sample preparation and analysis.

Re-extract samples with surrogate recoveries outside the limits on Table 6. If surrogate recoveries are acceptable after re-extraction, report the re-extraction results. If surrogate recoveries remain outside the quality control limits after re-extraction, assume the presence of a matrix interference; report the results of the initial analysis.

6.5 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

An MS/MSD must be prepared and analyzed with every twenty project samples of similar matrix and concentration.

When a sample requiring dilution has been chosen as the MS/MSD, the MS/MSD must be analyzed at the same dilution as the unspiked sample.

Calculate percent recovery as follows:

$$\text{Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Calculate the relative % difference (RPD) as follows:

$$RPD = \frac{2(D_1 - D_2)}{(D_1 + D_2)} \times 100$$

where D_1 = MS Result
D_2 = MSD Result

Advisory MS/MSD percent recovery and RPD limits are listed on Table 6. Since these limits are for advisory purposes only, they should not be used to determine if sample reanalysis is required.

6.6 METHOD DETECTION LIMIT (MDL) STUDIES

A method detection limit study is performed for water analysis annually according to the procedure in 40 CFR 136, Appendix B. The statistically-based MDLs obtained from the study must be less than or equal to the reporting limits for the method.

6.7 CONTROL LIMITS

The statistically-based control limits for precision and accuracy listed in Table 6 are updated periodically and, therefore, subject to chnage.

7.0 INTERFERENCES

7.1 Contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce carry over, the gas chromatographic column should be held at final temperature for an extended period of time, allowing saturated or late eluting compounds to be baked off. If an unusually concentrated example is encountered, it should be followed by analysis of a solvent blank to check for cross contamination.

7.2 Frequent replacement of the capillary injector liner helps to avoid chromatographic resolution problems.

7.3 Interferences can occur whenever a sample containing a high level of organics is analyzed. In some instances a dilution will be necessary, resulting in elevated detection limits. Low levels of target compounds may not be detectable due to the elevated detection limits.

8.0 SAFETY PRECAUTIONS

8.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

8.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

8.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

8.2 Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDS).

8.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

8.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

8.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

8.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

8.4 Handle all glass equipment with care, particularly during assembly and disassembly.

8.5 Avoid contact with hot GC parts (e.g., injection ports or transfer lines).

8.6 Vent GC/MS mechanical pump exhaust to the outside.

9.0 APPARATUS AND MATERIALS

9.1 EXTRACTION

9.1.1 Continuous liquid-liquid extractor: Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Corning "One-Step", or equivalent).

9.1.2 Drying column: 20-mm I.D. Pyrex chromatographic column. If so equipped, the stopcock material should be Teflon. Use columns without frits.

Transfer a small pad of Pyrex glass wool to the bottom of the column by tamping with a glass stirring rod or pipet. The glass wool retains the adsorbent in the column.

Pack the column with approximately 10 cm (about 3 inches) of anhydrous sodium sulfate. Put a funnel into the top of the column and pour the sodium sulfate into the column to the correct height.

Support the column in an upright position by means of a clamp attached to a metal ring stand. Prewash the column with approximately 50 mL methylene chloride followed by approximately 50 mL of the elution solvent if different from methylene chloride.

9.1.3 Kuderna-Danish (K-D) apparatus:

9.1.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Use a ground-glass stopper to prevent evaporation of the extract.

9.1.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, claps or safe-T joint.

9.1.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

9.1.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

9.1.4 Nitrogen blowdown module: Module (Reacti-therm from Pierce Chemical Company, Rockford, Illinois or equivalent) equipped with Luer-Lock blunt tip needles and a source of N_2 gas passed through an activated carbon column (Supelpure HC 2-2445 or equivalent). The module should accommodate aluminum blocks or a water bath to hold the concentrator tubes.

9.1.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or Teflon or equivalent).

9.1.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath must be used in a hood.

9.1.7 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap. Amber vials are preferred.

9.1.8 pH indicator paper: pH range including the desired extraction pH.

9.1.9 Heating mantle: Rheostat controlled. Alternatively, a hot plate may be used as a heating unit.

9.1.10 Syringe: 5-mL, or other suitable equipment to deliver small volumes of solvent for rinsing such as Pasteur pipets.

9.1.11 Graduated cylinder: 1-liter, 500-mL and 100-mL glass cylinders.

9.1.12 Plastic tubing: New plastic tubing must have the internal walls rinsed several times with hexane before use with the Reacti-therm heating module.

9.1..13 Erlenmeyer flask: 250-mL

9.1.14 Glass equipment supports: Ring stand or similar support with a clamp attached to support either the extractor body or the drying column.

9.1.15 Separatory funnel: 2-liter glass funnel with stopcock and stopper of Teflon.

9.1.16 Glass equipment supports: Ring stand with large metal ring attached to support the glass separatory funnel and a clamp attached to support the drying column in an upright position.

9.1.17 Sonicator and associated equipment:

9.1.17.1 **Sonicator**: Ultrasonic Cell Disrupter - horn-type sonicator with a minimum power wattage of 375 and pulsing capability (Heat Systems - Ultrasonics, Inc., Model W-385 [475 Watts] or equivalent). See Table 4 for daily tuning instructions.

9.1.17.2 **Sonicator Titanium Tips**: Tapped disrupter horns - ½-inch (No. 200) and ¾-inch (No. 207) (Heat Systems - Ultrasonics, Inc. or equivalent).

9.1.17.3 Sonicator Titanium Tips: Standard tapered 1/8-inch microtip ultrasonic probe (Heat Systems - Ultrasonics, Inc. or equivalent).

9.1.17.4 **Sonabox:** Optional damper box to contain sonicator during operation. (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

9.1.17.5 **Sonicator horn support equipment:** Vinyl-coated clamp attached to heavy-duty ring stand. Secure the clamp on the chrome housing of the sonicator convertor only. The movement of the horn will be restricted if the clamp is placed on the driver or the horn sections. The convertor may also be hand-held during use.

9.1.18 Balance: Top-loading, capable of weighing to 0.01 g.

9.1.19 Glass scintillation vials: At least 10-mL with Teflon-lined screw-cap.

9.1.20 Spatula: Stainless steel or Teflon.

9.1.21 Beakers: 400-mL.

9.1.22 Filtration apparatus:

9.1.22.1 **Glass funnel:** 80-mm or of sufficient size to contain filter paper.

9.1.22.2 **Filter paper:** Whatman No. 41 or equivalent.

9.2 ANALYSIS

9.2.1 Micro Syringes: 5-μL and larger, 0.006 inch ID needle.

9.2.2 Balance: Analytical, capable of weighing to 0.0001 grams.

9.2.3 Sample Vials: 2.0-ml, screw cap with Teflon liner.

9.2.4 Flasks: Class A, volumetric with ground glass stoppers.

9.2.5 GC column: 30 m x 0.32 mm ID bonded-phase silicone coated fused silica capillary column (J & W Scientific DB-5 or equivalent).

9.2.6 Gas Chromatography/Mass Spectrometer (GC/MS): Finnigan 4500/9610, Incos 50B or equivalent.

9.2.7 GC/MS Data System: Finnigan Mat - 1 INCOS or equivalent system equipped with Super Incos software.

9.2.8 Conical Autosampler Vials: Amber, 1-mL vials with crimp-top, teflon-lined caps.

10.0 REAGENTS

10.1 EXTRACTION

10.1.1 Reagent water: Deionized water passed through an activated carbon column.

10.1.2 Sodium hydroxide solution, 10 N: Dissolve 40 g ACS grade NaOH in reagent water. Dilute to 100 mL with reagent water.

10.1.3 Sodium sulfate: ACS grade granular, anhydrous. Purify by heating at 400°C for at least 4 hr in a shallow tray.

10.1.4 Sulfuric acid (H_2SO_4) solution (1:1): Slowly and with caution, add 50 mL of reagent grade H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

10.1.5 Extraction/exchange solvents: Methylene chloride, hexane, cyclohexane, acetonitrile. (See LSG Procedure AP-001, Reagent Screening, for grades and pre-screening procedure.)

10.1.6 Nitrogen (N_2) gas: Zero grade gas dried by filtering through a column of activated carbon.

10.1.7 Stock standards: Materials prepared from pure standard materials or purchased as certified solutions. Base/neutral and acid stock standards are prepared in methylene chloride.

Store stock standard solutions in Teflon-lined screw cap, glass containers at 4°C. Replace these solutions after six months or sooner if comparison with quality control check samples indicate a problem.

The spiking solution concentrations listed in Table 3 are approximate. **However, the exact concentration of each spiking solution must be accurately known.**

10.1.8 Clean sand: Reagent grade sand (e.g., Ottawa sand or sea sand) muffled at 400°C for 4 hours (minimum).

10.2 ANALYSIS

10.2.1 Reagent water: Deionized water passed through an activated carbon column.

10.2.2 Methylene chloride: Pesticide quality or equivalent.

10.2.3 Stock Standard Solutions: Stock standard solutions may be prepared from pure standard materials or purchased commercially. Prepare stock standard solutions in methylene chloride.

10.2.4 Calibration standards: Prepare calibration standards containing each target semivolatile compound (see Tables 1 and 2) and surrogate standard at five concentration levels from stock solutions: 20, 50, 80, 120, and 160 µg/mL. Each solution must also contain internal standards at 40 µg/mL.

10.2.5 Surrogate, Internal and Matrix Spiking Standard Solutions: Prepare the indicated solutions as follows:

10.2.5.1 **Surrogate Standard Spiking Solution** - Prepare LLW, LLS, and MLS surrogate spiking solutions at the indicated concentrations from stock in methanol.

Compound	LLW, LLS and MLS
Nitrobenzene-d_5	100 µg/mL
2-Fluorobiphenyl	100 µg/mL
p-Terphenyl-d_{14}	100 µg/mL
Phenol-d_5	200 µg/mL
2-Fluorophenol	200 µg/mL
2,4,6-Tribromophenol	200 µg/mL

10.2.5.2 **Internal Standard Spiking Solution** - Prepare a 800 µg/mL solution containing the following compounds in methylene chloride.

1,4-Dichlorobenzene-d_4	Phenanthrene-d_{10}
Naphthalene-d_8	Chrysene-d_{12}
Acenaphthene-d_{10}	Perylene-d_{12}

10.2.5.3 **DFTPP Solution** - Prepare a solution containing the following compound in methylene chloride:

Decafluorotriphenylphosphene (DFTPP)	50 µg/mL

10.2.5.4 **BNA Matrix Spiking Solutions** - Prepare solutions containing the following compounds at the indicated concentrations in methanol.

Base/Neutrals (100 µg/mL)	Acids (200 µg/mL)
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Benzo(a)pyrene	2-Nitrophenol
di-n-octyl phthalate	2,4,6-trichlorophenol
fluoranthene	
hexachlorobutadiene	

11.0 REFERENCES

11.1 U.S. EPA SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Volume IB, 1986; Methods 3500, 3510, 3520, 3550, and 8270.

11.2 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984, Method 625.

11.3 U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM01.8

TABLE 1

Semivolatile Oganics Reporting Limits for TCL and Priority Pollutant Analyses

Parameter	Water ug/L	Soil ug/Kg
acenephthene	10	330
acenaphthylene	10	330
anthracene	10	330
benzidine	50	1600
benzo(a)anthracene	10	330
benzo(a)pyrene	10	330
benzo(b)fluoranthene	10	330
benzo(g,h,i)perylene	10	330
benzo(k)fluoranthene	10	330
benzoic acid	50	1600
benzyl alcohol	10	330
bis(2-chloroethoxy)methane	10	330
bis(2-chloroethyl)ether	10	330
2,2'-oxybis(1-chloropropane)	10	330
bis(2-ethylhexyl)phthalate	10	330
butylbenzylphthalate	10	330
4-bromophenylphenyl ether	10	330
carbazole	10	330
4-chloroaniline	10	330
2-chloronaphthalene	10	330
4-chlorophenyl phenyl ether	10	330
chrysene	10	330
dibenz(a,h)anthracene	10	330
dibenzofuran	10	330
1,2-dichlorobenzene	10	330
1,3-dichlorobenzene	10	330
1,4-dichlorobenzene	10	330
3,3'-dichlorobenzidine	20	660
diethylphthalate	10	330
dimethylphthalate	10	330
di-n-butylphthalate	10	330
di-n-octylphthalate	10	330
2,4-dinitrotoluene	10	330
2,6-dinotrotoluene	10	330
1,2-diphenylhydrazine	10	330
fluoranthene	10	330
fluorene	10	330
hexachlorobenzene	10	330
hexachlorobutadiene	10	330

Table 1
Semivolatile Organics Reporting Limits for TCL and Priority Pollutant Analyses (cont'd)
Page Two

Parameter	Water ug/L	Soil ug/Kg
hexachlorocyclopentadiene	10	330
hexachloroethane	10	330
indeno(1,2,3-cd)pyrene	10	330
isophorone	10	330
2-methylnaphthalene	10	330
naphthalene	10	330
2-nitroanaline	50	1600
3-nitroanaline	50	1600
4-nitroanaline	50	1600
nitrobenzene	10	330
N-nitrosodimethylamine	10	330
N-nitroso-di-n-propylamine	10	330
N-nitrosodiphenylamine	10	330
phenanthrene	10	330
pyrene	10	330
1,2,4-trichlorobenzene	10	330
4-chloro-3-methylphenol	10	330
2-chlorophenol	10	330
2,4-dichlorophenol	10	330
2,4-dimethylphenol	10	330
2,4-dinitrophenol	50	1600
4,6-dinitro-2-methylphenol	50	1600
2-methylphenol	10	330
4-methylphenol	10	330
2-nitrophenol	10	330
4-nitrpohenol	50	1600
pentachlorophenol	50	1600
phenol	10	330
2,4,5-trichlorophenol	50	1600
2,4,6-trichlorophenol	10	330

TABLE 2

Semivolatile Oganics Reporting Limits for Residential Well Analyses

Parameter	Target PQL ug/L	Cont. MDL ug/L	SF MDL ug/L
acenephthene	5	7	6
acenaphthylene	5	8	6
anthracene	5	6	5
benzo(a)anthracene	5	9	5
benzo(a)pyrene	5	7	6
benzo(b)fluoranthene	5	2	7
benzo(g,h,i)perylene	5	8	9
benzo(k)fluoranthene	5	8	10
benzyl alcohol	5	6	9
bis(2-chloroethoxy)methane	5	6	8
2,2'-oxybis(1-chloropropane)	5	4	10
bis(2-chloroisopropyl)ether	5	6	9
bis(2-ethylhexyl)phthalate	5	8	4
butylbenzylphthalate	5	8	5
4-bromophenylphenyl ether	5	6	6
4-chloroaniline	5	5	8
2-chloronaphthalene	5	6	7
4-chlorophenyl phenyl ether	5	7	6
chrysene	5	7	6
dibenz(a,h)anthracene	5	8	9
dibenzofuran	5	7	7
1,2-dichlorobenzene	5	10	8
1,3-dichlorobenzene	5	9	8
1,4-dichlorobenzene	5	20	8
3,3'-dichlorobenzidine	20	10	7
diethylphthalate	5	20	10
dimethylphthalate	5	20	20
di-n-butylphthalate	5	6	6
di-n-octylphthalate	5	9	7
2,4-dinitrotoluene	5	7	7
2,6-dinotrotoluene	5	7	6
fluoranthene	5	7	7
fluorene	5	8	5
hexachlorobenzene	5	7	6
hexachlorobutadiene	5	9	7
hexachlorocyclopentadiene	5	3	7
hexachloroethane	5	20	7
indeno(1,2,3-cd)pyrene	5	7	4

Table 2
Semivolatile Organics Detection Limits for Residential Well Analyses (cont'd)
Page Two

Parameter	Target PQL ug/L	Cont. MDL ug/L	SP MDL ug/L
isophorone	5	5	8
2-methylnaphthalne	5	7	6
naphthalene	5	9	7
2-nitroaniline	20	7	6
3-nitroaniline	20	10	6
4-nitroaniline	20	20	8
nitrobenzene	5	6	9
N-nitroso-di-n-propylamine	5	6	8
N-nitrosodiphenylamine	5	7	6
phenanthrene	5	8	5
pyrene	5	7	5
1,2,4-trichlorobenzene	5	8	7
benzoic acid	5	30	20
4-chloro-3-methylphenol	5	4	5
2-chlorophenol	5	3	9
2,4-dichlorophenol	5	3	8
2,4-dimethylphenol	5	2	4
2,4-dinitrophenol	20	20	20
4,6-dinitro-2-methylphenol	20	6	10
2-methylphenol	5	4	8
4-methylphenol	5	4	7
2-nitrophenol	5	3	7
4-nitrpohenol	20	20	8
pentachlorophenol	20	4	7
phenol	5	3	6
2,4,5-trichlorophenol	20	5	7
2,4,6-trichlorophenol	5	4	7

TABLE 3

Spiking Solutions

Test	QC Solution	Solvent	Sample Matrix: Spike Added	Analyte(s)	Concentration of Spike Solution*
GC/MS BNAs	Surrogate Spike	Methanol	Water: 1.0 mL/1000 mL sample[1] LLS: 0.5 mL/30 g sample[1] MLS: 1.0 mL/1 g sample[1] Soxhlet: 0.5 mL/10 g sample[1]	2-Fluorobiphenyl Nitrobenzene-d_5 Terphenyl-d_{14} 2-Fluorophenol 2,4,6-Tribromophenol Phenol-d_5	100 µg/mL 100 µg/mL 100 µg/mL 200 µg/mL 200 µg/mL 200 µg/mL
GC/MS BNAs	Matrix Spike	Methanol	Water: 1.0 mL/1000 mL sample[1] LLS: 0.5 mL/30 g sample[1] MLS: 1.0 mL/1 g sample[1] Soxhlet: 0.5 mL/10 g sample[1]	1,2,4-Trichlorobenzene Acenaphthene 2,4-Dinitrotoluene Pyrene N-nitroso-di-n-propylamine 1,4-Dichlorobenzene Pentachlorophenol Phenol 2-Chlorophenol 4-Chloro-3-methyl phenol 4-Nitrophenol	100 µg/mL 100 µg/mL 100 µg/mL 100 µg/mL 100 µg/mL 100 µg/mL 200 µg/mL 200 µg/mL 200 µg/mL 200 µg/mL 200 µg/mL
GC/MS BNAs	NPDES (Region III) Matrix Spike	Methanol	Water: 1.0 mL/1000 mL sample	All BNA priority pollutants	100 µg/mL

TABLE 4

Tuning Procedures for Ultrasonic Cell Disrupter, Model W-385

Tune the sonicator daily as follows:

1. Place power switch (ON/OFF/TUNE) in the "OFF" position.

2. Turn the timer to the "HOLD" position.

3. Turn the output control knob fully counter-clockwise, below setting "1" for minimum amplitude.

4. Push and hold the power switch down in the "TUNE" position (it is spring loaded in this position and must be held during tuning).

5. Slowly turn the output control knob to setting "10" (maximum amplitude) taking care not to exceed 100%.

   - If the meter approaches 100%, lower the control knob setting to about "5" and continue with steps 6 through 9. Then raise the setting to "10" and retune.

   - If the generator has been thrown far off resonance, several increments between settings "5" and "10" may be required before the knob can be set to "10" without exceeding 100% on the meter.

6. Turn the tuning knob in whichever direction will cause the meter needle to move toward zero (0).

7. Continue turning the tuning knob in that same direction until the needle stops moving and then begins to move in a reverse direction.

8. Reverse the tuning knob very slowly to return the meter needle to its lowest reading (that "null" point at which any motion of the tuning knob in either direction will cause the needle to deflect away from zero).

9. Return the output control knob to minimum setting (fully counter-clockwise) and release the power switch. The generator is now tuned properly.

TABLE 5

Internal Standard Assignments

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenol	Nitrobenzene	Hexachlorocyclo-pentadiene	4,6-Dinitro-2-methylphenol	Pyrene	Di-n-octyl-phthalate
bis(2-Chloroethyl)ether	Isophorone	2-4-6-Trichlorophenol	N-Nitrosodiphenyl-amine	Butylbenzylphthalate	Benzo(b)fluoranthene
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol	1,2-Diphenylhydrazine	3,3-Dichlorobenzidine	Benzo(k)fluoranthene
1,3-Dichlorobenzene	2,4-Dimethyl-phenol	2-Chloronaphthalene	4-Bromophenyl-phenylether	Benzo(a)anthracene	Benzo(a)pyrene
1,4-Dichlorobenzene	Benzoic acid	2-Nitroaniline	Hexachlorobenzene	bis(2-Ethylhexyl)-phthalate	Indeno(1,2,3-cd) pyrene
Benzyl alcohol	bis(2-Chloroethoxy) methane	Dimethylphthalate	Pentachlorophenol	Chrysene	Dibenz(a,h) anthracene
1,2-Dichlorobenzene	2,4-Dichlorophenol	Acenaphthylene	Phenanthrene	Benzidine	Benzo(g,h,i)perylene
2-Methylphenol	1,2,4-Trichloro-benzene	3-Nitroaniline	Anthracene	Terphenyl-d_{14} (surr)	
2,2'-oxybis (1-Chloropropane)	Naphthalene	Acenaphthene	Di-n-butyl-phthalate		
4-Methylphenol	4-Chloroaniline	2,4-Dinitrophenol	Fluoranthene		
N-Nitroso-di-n propylamine	Hexachlorobutadiene	4-Nitrophenol			
Hexachloroethane	4-Chloro-3-methylphenol	Dibenzofuran			
bis(2-Chloroisopropyl) ether	2-Methylnaphthalene	2,4-Dinitrotoluene			
N-Nitrosodimethyl-amine	Nitrobenzene-d_5 (surr)	2,6-Dinitrotoluene			
2-Fluorophenol (surr)		Diethylphthalate			
Phenol-d_6 (surr)		4-Chlorophenyl-phenylether			
		Fluorene			
		4-Nitroaniline			
		2-Fluorobiphenyl (surr)			
		2,4,6-Tribromophenol (surr)			

Surr = surrogate compound

TABLE 6

QC Limits

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E27% AM: O10W
SEPARATORY FUNNEL

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
1,2,4-trichlorobenzene	OL35	≤19.5	≤25.8	6.92	6.29	-	33.8-89.1	20.0-103	61.43	13.82	-	47.1-88.3	36.8-98.6	67.69	10.31
1,2-dichlorobenzene	OL41	≤21.3	≤27.5	8.82	6.23	-	42.6-76.8	34.1-85.3	59.70	8.54	-	-	-	-	-
1,3-dichlorobenzene	OL45	≤24.0	≤31.1	9.71	7.12	-	39.4-75.8	30.3-85.0	57.65	9.10	-	-	-	-	-
1,4-dichlorobenzene	OL47	≤21.9	≤29.1	7.59	7.16	-	25.1-77.3	12.1-90.4	51.24	13.05	-	33.4-84.7	20.5-97.5	59.05	12.83
2,4,5-trichlorophenol	OM05	≤29.8	≤40.8	7.76	11.01	-	55.3-103	43.4-115	79.20	11.94	-	-	-	-	-
2,4,6-trichlorophenol	OM07	≤8.49	≤10.8	3.81	2.34	-	47.2-102	33.4-116	74.68	13.75	-	-	-	-	-
2,4-dichlorophenol	OM08	≤9.45	≤12.5	3.29	3.08	-	61.6-92.5	53.8-100	77.04	7.73	-	-	-	-	-
2,4-dimethylphenol	OM09	≤7.92	≤10.6	2.62	2.65	-	58.0-94.4	49.0-103	76.22	9.09	-	-	-	-	-
2,4-dinitrophenol	OM10	≤31.2	≤40.7	12.07	9.54	-	24.5-103	4.91-123	63.77	19.62	-	-	-	-	-
2,4-dinitrotoluene	OM11	≤18.4	≤24.2	6.76	5.80	-	55.9-98.6	45.3-109	77.27	10.67	-	57.5-102	46.4-113	79.84	11.16
2,6-dinitrotoluene	OM13	≤16.7	≤22.2	5.78	5.46	-	69.2-96.7	62.4-104	82.96	6.87	-	-	-	-	-
2-chloronaphthalene	OM15	≤18.8	≤24.8	6.65	6.05	-	63.6-92.4	56.4-99.6	77.96	7.20	-	-	-	-	-
2-chlorophenol	OM16	≤14.0	≤18.6	4.84	4.58	-	48.8-91.5	38.2-102	70.19	10.67	-	47.8-88.6	37.6-98.7	68.19	10.18
2-methyl-4,6-dinitrophenol	OM20	≤41.6	≤55.3	14.15	13.75	-	32.5-107	13.9-125	69.65	18.59	-	-	-	-	-
2-methylnaphthalene	OM22	≤17.3	≤22.7	6.36	5.46	-	59.1-88.4	51.8-95.7	73.71	7.32	-	-	-	-	-
2-methylphenol	OM23	≤14.5	≤19.1	5.45	4.54	-	47.5-95.1	35.6-107	71.28	11.91	-	-	-	-	-
2-nitroaniline	OM25	≤24.9	≤32.7	9.31	7.80	-	59.0-106	47.2-118	82.54	11.77	-	-	-	-	-
2-nitrophenol	OM26	≤8.84	≤11.3	3.84	2.50	-	62.2-88.3	55.6-94.8	75.23	6.54	-	-	-	-	-
3,3'-dichlorobenzidine	OM29	≤22.9	≤30.0	8.80	7.05	-	67.2-106	57.6-115	86.42	9.62	-	-	-	-	-
3,4-benzofluoranthene [Benzo(b)fluoranthene]	OM33	≤21.5	≤28.0	8.64	6.44	-	51.7-96.4	40.6-108	74.04	11.16	-	-	-	-	-
3-nitroaniline	OM37	≤24.4	≤31.8	9.44	7.46	-	61.5-98.6	52.3-108	80.08	9.27	-	-	-	-	-
4-bromophenyl phenyl ether	OM39	≤13.0	≤17.0	5.15	3.94	-	61.3-95.6	52.7-104	78.42	8.57	-	-	-	-	-

Table 6
QC Limits (cont'd)
Page Two

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E27%; AM: 010W
SEPARATORY FUNNEL

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
4-chloro-3-methylphenol	OM40	≤10.9	≤14.3	4.14[3]	3.40[3]	-	57.8-96.6	48.1-106	77.17	9.69	-	56.4-93.9	47.0-103	75.16	9.38
4-chloroaniline	OM41	≤25.9	≤34.6	8.37[3]	8.76[3]	-	62.7-88.2	56.4-94.5	75.46	6.36	-	-	-	-	-
4-chlorophenyl phenyl ether	OM42	≤16.2	≤21.5	5.51[3]	5.33[3]	-	66.0-98.4	57.9-106	82.17	8.10	-	-	-	-	-
4-methylphenol	OM43	≤15.3	≤19.9	5.97[3]	4.65[3]	-	48.7-92.3	37.8-103	70.48	10.91	-	-	-	-	-
4-nitroaniline	OM44	≤25.0	≤33.2	8.59[3]	8.21[3]	-	53.1-112	38.5-126	82.33	14.60	-	-	-	-	-
4-nitrophenol	OM45	≤20.5	≤26.5	8.38[3]	6.05[3]	-	19.3-91.4	1.30-109	55.39	18.03	-	17.5-94.6	-1.75-114	56.03	19.26
N-nitroso-di-n-propylamine	ON02	≤18.8	≤25.2	6.11	6.36	-	59.4-89.4	51.9-96.9	74.39	7.49	-	52.3-104	39.5-116	77.98	12.82
N-nitrosodiphenylamine	ON05	-	≤20.0[6]	-	-	-	60.8-91.6	53.2-99.2	76.21	7.68	-	-	-	-	-
acenaphthene	ON13	≤15.0	≤19.9	5.28	4.87	-	54.9-95.2	44.8-105	75.02	10.07	-	56.7-93.5	47.4-103	75.10	9.22
acenaphthylene	ON14	≤18.2	≤24.2	6.08[3]	6.05[3]	-	68.1-97.6	60.8-105	82.83	7.36	-	-	-	-	-
anthracene	ON19	≤12.6	≤16.4	5.07[3]	3.76[3]	-	64.6-103	55.0-113	83.83	9.61	-	-	-	-	-
benzo(a)anthracene	ON23	≤16.7	≤21.9	6.38[3]	5.18[3]	-	66.1-101	57.3-110	83.67	8.79	-	-	-	-	-
benzo(a)pyrene	ON24	≤21.7	≤28.1	8.81[3]	6.42[3]	-	56.4-97.6	46.1-108	77.00	10.30	-	-	-	-	-
benzo(g,h,i)perylene	ON25	≤86.0	≤118	21.2[3]	32.4[3]	-	54.1-112	39.7-126	82.88	14.38	-	-	-	-	-
benzo(k)fluoranthene	ON27	≤22.1	≤28.8	8.68[3]	6.70[3]	-	55.4-109	42.0-122	82.17	13.40	-	-	-	-	-
benzoic acid	ON28	≤62.3	≤80.0	27.00[3]	17.66[3]	-	10.3-60.6	-2.3-73.2	35.47[5]	12.59[5]	-	-	-	-	-
benzyl alcohol	ON29	0.67-8.51	≤10.5	4.59[3]	1.96[3]	-	42.9-93.2	30.3-106	68.05[6]	17.36[6]	-	-	-	-	-
benzyl butyl phthalate	ON30	≤12.4	≤16.1	5.01[3]	3.70[3]	-	61.9-105	51.2-116	83.46	10.76	-	-	-	-	-
bis(2-chloroethoxy)methane	ON33	≤19.0	≤25.3	6.29[3]	6.33[3]	-	65.9-88.6	60.2-94.2	77.22	5.67	-	-	-	-	-
bis(2-chloroethyl)ether	ON34	≤20.8	≤27.1	8.09[3]	6.33[3]	-	59.9-91.5	52.1-99.3	75.70	7.88	-	-	-	-	-
bis(2-chloroisopropyl)ether	ON35	≤19.1	≤24.7	7.96[3]	5.58[3]	-	-	22.0-179[7]	-	-	-	-	-	-	-
bis(2-ethylhexyl)phthalate	ON36	≤16.4	≤21.8	5.53[3]	5.41[3]	-	57.2-104	45.4-116	80.67	11.75	-	-	-	-	-

Table 6
QC Limits (cont'd)
Page Three

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E27% AM: 010W
SEPARATORY FUNNEL

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
carbazole		-	≤20.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
chrysene	ON39	≤11.0	≤14.0	4.95[3]	3.04[3]	-	67.0-99.2	59.0-107	83.08	8.04	-	-	-	-	-
di-n-butyl phthalate	ON41	≤11.2	≤14.6	4.40[3]	3.41[3]	-	63.3-97.4	54.8-106	80.38	8.53	-	-	-	-	-
di-n-octyl phthalate	ON42	≤20.4	≤26.3	8.69[3]	5.88[3]	-	47.0-102	33.3-116	74.42	13.70	-	-	-	-	-
dibenz(a,h)anthracene	ON44	0.10-13.4	≤16.7	6.27[3]	3.32[3]	-	52.8-101	40.7-114	77.13	12.14	-	-	-	-	
dibenzofuran	ON47	≤16.4	≤21.9	5.48[3]	5.48[3]	-	70.3-92.9	64.7-98.6	81.61	5.65	-	-	-	-	-
diethyl phthalate	ON48	≤27.5	≤36.7	29.25[3]	49.13[3]	-	49.9-100	37.2-113	75.13	12.63	-	-	-	-	-
dimethyl phthalate	ON50	≤34.2	≤44.2	14.12[3]	10.01[3]	-	10.4-99.9	-12.0-122	55.13	22.37	-	-	-	-	-
fluoranthene	0003	≤14.7	≤18.7	6.66[3]	4.01[3]	-	62.8-98.9	53.7-108	80.83	9.03	-	-	-	-	-
fluorene	0004	≤16.8	≤22.3	5.81[3]	5.49[3]	-	69.0-99.5	61.4-107	84.25	7.62	-	-	-	-	-
hexachlorobenzene	0005	≤18.6	≤24.9	5.93[3]	6.31[3]	-	61.0-97.4	51.9-106	79.18	9.09	-	-	-	-	-
hexachlorobutadiene	0006	≤19.5	≤25.1	8.32[3]	5.60[3]	-	18.2-99.0	-1.94-119	58.63	20.19	-	-	-	-	-
hexachlorocyclopentadiene	0007	≤17.5	≤22.4	7.76[3]	4.87[3]	-	49.4-87.5	39.8-97.0	68.43	9.54	-	-	-	-	-
hexachloroethane	0008	≤23.0	≤29.4	10.17[3]	6.42[3]	-	17.1-86.0	-0.08-103	51.58	17.22	-	-	-	-	-
indeno(1,2,3-cd)pyrene	0013	≤18.5	≤23.6	8.20[3]	5.15[3]	-	53.2-103	40.7-116	78.33	12.55	-	-	-	-	-
isophorone	0015	≤19.2	≤25.4	6.68[3]	6.19[3]	-	60.5-94.9	51.9-104	77.70	8.60	-	-	-	-	-
naphthalene	0019	≤14.5	≤18.3	7.08[3]	3.73[3]	-	58.4-91.0	50.3-99.1	74.71	8.14	-	-	-	-	-
nitrobenzene	0020	≤20.7	≤26.8	8.41[3]	6.13[3]	-	57.4-90.3	49.1-98.5	73.81	8.23	-	-	-	-	-
pentachlorophenol	0027	≤30.9	≤41.1	10.41	10.23	-	24.0-120	0.11-144	71.93	23.94	-	7.03-122	-21.6-150	64.35	28.66
phenanthrene	0029	≤11.6	≤14.8	5.19[3]	3.19[3]	-	64.9-96.3	57.0-104	80.58	7.85	-	-	-	-	-
phenol	0030	≤16.6	≤21.9	5.96[3]	5.32[3]	-	32.1-70.1	22.6-79.6	51.13	9.50	-	24.3-62.5	14.7-72.0	43.36	9.55
pyrene	0033	≤19.6	≤26.2	6.36	6.62	-	63.0-114	50.4-126	88.31	12.63	-	53.4-110	39.2-125	81.87	14.24

Table 6
QC Limits (cont'd)
Page Four

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E27% AM: 0104
SEPARATORY FUNNEL

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
2,4,6-tribromophenol (S)	0M06	NA	NA	NA	NA	NA	15.1-106	-7.69-129	60.65	22.78	-	NA	NA	NA	NA
2-fluorobiphenyl (S)	0M17	NA	NA	NA	NA	NA	38.8-81.5	28.1-92.2	60.12	10.68	-	NA	NA	NA	NA
2-fluorophenol (S)	0M18	NA	NA	NA	NA	NA	15.2-83.0	-1.78-99.9	49.07	16.95	-	NA	NA	NA	NA
nitrobenzene-d5 (S)	0021	NA	NA	NA	NA	NA	26.0-98.0	8.06-116	62.03	17.99	-	NA	NA	NA	NA
p-terphenyl-d14 (S)	0024	NA	NA	NA	NA	NA	38.7-104	22.5-120	71.20	16.24	-	NA	NA	NA	NA
phenol-d5 (S)	0031	NA	NA	NA	NA	NA	15.5-58.6	4.68-69.4	37.02	10.78	-	NA	NA	NA	NA

3 DATA CALCULATED 12/92.

Table 6
QC Limits (cont'd)
Page Five

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E29% AM: 010W
CONTINUOUS EXTRACTION

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
1,2,4-trichlorobenzene		-	<20.0[6]	-	-	-	-	33.3-153[7]	-	-	-	-	-	-	-
1,2-dichlorobenzene								21.3-139[7]							
1,3-dichlorobenzene								-20.0-191[7]							
1,4-dichlorobenzene								8.22-135[7]							
2,4,5-trichlorophenol								25-125[4]							
2,4,6-trichlorophenol								25.4-156[7]							
2,4-dichlorophenol								28.3-145[7]							
2,4-dimethylphenol								21.7-129[7]							
2,4-dinitrophenol								-95.2-221[7]							
2,4-dinitrotoluene								27.8-147[7]							
2,6-dinitrotoluene								43.0-162[7]							
2-chloronaphthalene								53.3-125[7]							
2-chlorophenol								9.62-147[7]							
2-methyl-4,6-dinitrophenol								-52.6-205[7]							
2-methylnaphthalene								25-125[4]							
2-methylphenol								25-125[4]							
2-nitroaniline								25-125[4]							
2-nitrophenol								25-125[8]							
3,3'-dichlorobenzidine								-55.6-276[7]							
3,4-benzofluoranthene [Benzo(b)fluoranthene]								8.98-173[7]							
3-nitroaniline								25-125[4]							
4-bromophenyl phenyl ether								44.6-135[7]							

Table 6
QC Limits (cont'd)
Page Six

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E29%; AM: O10W
CONTINUOUS EXTRACTION

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
4-chloro-3-methylphenol		-	<20.0[6]	-	-	-	-	7.0-162[7]	-	-	-	-	-	-	-
4-chloroaniline								25-125[4]							
4-chlorophenyl phenyl ether								10.5-173[7]							
4-methylphenol								25-125[4]							
4-nitroaniline								25-125[4]							
4-nitrophenol								-28.8-148[7]							
N-nitroso-di-n-propylamine								-35.3-247[7]							
N-nitrosodiphenylamine								25-125[4]							
acenaphthene								37.6-155[7]							
acenaphthylene								21.4-158[7]							
anthracene								17.2-144[7]							
benzo(a)anthracene								19.9-155[7]							
benzo(a)pyrene								-0.46-180[7]							
benzo(g,h,i)perylene								-50.2-244[7]							
benzo(k)fluoranthene								-5.47-176[7]							
benzoic acid								25-125[4]							
benzyl alcohol								25-125[4]							
benzyl butyl phthalate								-40.7-169[7]							
bis(2-chloroethoxy)methane								17.5-196[7]							
bis(2-chloroethyl)ether								-4.52-173[7]							
bis(2-chloroisopropyl)ether								22.0-179[7]							
bis(2-ethylhexyl)phthalate								-8.64-174[7]							

Table 6
QC Limits (cont'd)
Page Seven

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E29% AM: 0100

CONTINUOUS EXTRACTION

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
carbazole		-	<20.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
chrysene								1.19-183[7]							
di-n-butyl phthalate								-20.0-131[7]							
di-n-octyl phthalate								-11.8-162[7]							
dibenz(a,h)anthracene								-72.1-258[7]							
dibenzofuran								25-125[4]							
diethyl phthalate								-25.3-113[7]							
dimethyl phthalate								-42.4-84.5[7]							
fluoranthene								14.9-149[7]							
fluorene								53.1-127[7]							
hexachlorobenzene								-20.1-169[7]							
hexachlorobutadiene								13.9-126[7]							
hexachlorocyclopentadiene								25-125[4]							
hexachloroethane								33.0-111[7]							
indeno(1,2,3-cd)pyrene								-36.1-186[7]							
isophorone								0.35-226[7]							
naphthalene								9.80-145[7]							
nitrobenzene								19.5-192[7]							
pentachlorophenol								-3.49-195[7]							
phenanthrene								47.1-127[7]							
phenol								-3.49-92.5[7]							
pyrene								45.2-122[7]							

Table 6
QC Limits (cont'd)
Page Eight

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
WATER
PM: E29% AM: 010W
CONTINUOUS EXTRACTION

COMPOUND	COMBO	PRECISION AS RPD					PERCENT RECOVERY OF LAB CONTROL STANDARDS					PERCENT RECOVERY OF MATRIX SPIKES			
		WL	CL	X	S	CPK[1]	WL	CL	X	S	CPK[2]	95% CI	99% CI	X	S
2,4,6-tribromophenol (S)		NA				→	-	10-123 [9]	-	-	-	NA			→
2-fluorobiphenyl (S)		NA				→	↓	43-116 [9]	↓	↓	↓	NA			→
2-fluorophenol (S)		NA				→		21-100 [9]				NA			→
nitrobenzene-d5 (S)		NA				→		35-114 [9]				NA			→
p-terphenyl-d14 (S)		NA				→		33-141 [9]				NA			→
phenol-d5 (S)		NA				→	↓	10-94 [9]	↓	↓	↓	NA			

Table 6
QC Limits (cont'd)
Page Nine

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
SOIL
PM: E30% AM: 010S%

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
1,2,4-trichlorobenzene	0139	≤14.6	≤19.6	4.60	4.99	-	60.9-96.2	52.0-105	78.51	8.82	-	64.4-100	55.5-109	82.33	8.94
1,2-dichlorobenzene	0141	-	≤40.0[6]	-	-	-	-	21.3-139[7]	-	-	-	-	-	-	-
1,3-dichlorobenzene	0144	-	≤40.0[6]	-	-	-	-	-20.0-191[7]	-	-	-	-	-	-	-
1,4-dichlorobenzene	0146	≤17.6	≤23.4	5.83	5.87	-	53.0-93.5	43.0-104	73.28	10.09	-	56.5-91.3	47.8-100	73.94	8.70
2,4,5-trichlorophenol	0J04	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
2,4,6-trichlorophenol	0J06	-	≤40.0[6]	-	-	-	-	25.4-156[7]	-	-	-	-	-	-	-
2,4-dichlorophenol	0J07	-	≤40.0[6]	-	-	-	-	28.3-145[7]	-	-	-	-	-	-	-
2,4-dimethylphenol	0J08	-	≤40.0[6]	-	-	-	-	21.7-129[7]	-	-	-	-	-	-	-
2,4-dinitrophenol	0J09	-	≤40.0[6]	-	-	-	-	-95.2-221[7]	-	-	-	-	-	-	-
2,4-dinitrotoluene	0J10	≤17.6	≤23.5	5.87	5.87	-	51.6-108	37.4-122	79.92	14.17	-	50.7-111	35.5-127	81.11	15.19
2,6-dinitrotoluene	0J12	-	≤40.0[6]	-	-	-	-	43.0-162[7]	-	-	-	-	-	-	-
2-chloronaphthalene	0J14	-	≤40.0[6]	-	-	-	-	53.3-125[7]	-	-	-	-	-	-	-
2-chlorophenol	0J15	≤11.9	≤15.7	4.31	3.81	-	57.8-100	47.2-111	78.94	10.59	-	60.1-102	49.5-113	81.13	10.53
2-methyl-4,6-dinitrophenol	0J19	-	≤40.0[6]	-	-	-	-	-52.6-205[7]	-	-	-	-	-	-	-
2-methylnaphthalene	0J21	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
2-methylphenol	0J22	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
2-nitroaniline	0J24	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
2-nitrophenol	0J25	-	≤40.0[6]	-	-	-	-	25-125[8]	-	-	-	-	-	-	-
3,3'-dichlorobenzidine	0J28	-	≤40.0[6]	-	-	-	-	-55.6-276[7]	-	-	-	-	-	-	-
3,4-benzofluoranthene [Benzo(b)fluoranthene]	0J30	-	≤40.0[6]	-	-	-	-	8.98-173[7]	-	-	-	-	-	-	-
3-nitroaniline	0J34	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
4-bromophenyl phenyl ether	0J36	-	≤40.0[6]	-	-	-	-	44.6-135[7]	-	-	-	-	-	-	-

Table 6
QC Limits (cont'd)
Page Ten

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
SOIL
PM: E30% AM: 010S%

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
4-chloro-3-methylphenol	0J37	≤19.7	≤26.6	5.96	6.87	-	58.8-104	47.6-115	81.39	11.28	-	60.7-107	49.0-119	84.07	11.69
4-chloroaniline	0J38	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
4-chlorophenyl phenyl ether	0J39	-	≤40.0[6]	-	-	-	-	10.5-173[7]	-	-	-	-	-	-	-
4-methylphenol	0J40	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
4-nitroaniline	0J41	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
4-nitrophenol	0J42	≤32.4	≤43.8	9.64	11.37	-	44.4-97.0	31.2-110	70.67	13.15	-	38.5-113	19.8-132	75.79	18.66
N-nitroso-di-n-propylamine	0J47	≤15.0	≤20.0	5.03	4.99	-	52.9-113	37.8-128	82.88	15.01	-	54.0-114	38.9-129	84.21	15.09
N-nitrosodiphenylamine	0J50	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
acenaphthene	0K07	≤15.5	≤20.6	5.23	5.12	-	55.4-106	42.8-119	80.75	12.65	-	64.0-106	53.6-116	84.96	10.47
acenaphthylene	0K08	-	≤40.0[6]	-	-	-	-	21.4-158[7]	-	-	-	-	-	-	-
anthracene	0K13	-	≤40.0[6]	-	-	-	-	17.2-144[7]	-	-	-	-	-	-	-
benzo(a)anthracene	0K17	-	≤40.0[6]	-	-	-	-	19.9-155[7]	-	-	-	-	-	-	-
benzo(a)pyrene	0K18	-	≤40.0[6]	-	-	-	-	-0.46-180[7]	-	-	-	-	-	-	-
benzo(g,h,i)perylene	0K19	-	≤40.0[6]	-	-	-	-	-50.2-244[7]	-	-	-	-	-	-	-
benzo(k)fluoranthene	0K21	-	≤40.0[6]	-	-	-	-	-5.47-176[7]	-	-	-	-	-	-	-
benzoic acid	0K22	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
benzyl alcohol	0K23	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
benzyl butyl phthalate	0K24	-	≤40.0[6]	-	-	-	-	-40.7-169[7]	-	-	-	-	-	-	-
bis(2-chloroethoxy)methane	0K26	-	≤40.0[6]	-	-	-	-	17.5-196[7]	-	-	-	-	-	-	-
bis(2-chloroethyl)ether	0K27	-	≤40.0[6]	-	-	-	-	-4.52-173[7]	-	-	-	-	-	-	-
bis(2-chloroisopropyl)ether	0K28	-	≤40.0[6]	-	-	-	-	22.0-179[7]	-	-	-	-	-	-	-
bis(2-ethylhexyl)phthalate	0K29	-	≤40.0[6]	-	-	-	-	-8.64-174[7]	-	-	-	-	-	-	-

Table 6
QC Limits (cont'd)
Page Eleven

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
SOIL
PM: E30X AM: O10SX

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
carbazole		-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
chrysene	OK30	-	≤40.0[6]	-	-	-	-	1.19-183[7]	-	-	-	-	-	-	-
di-n-butyl phthalate	OK33	-	≤40.0[6]	-	-	-	-	-12.0-131[7]	-	-	-	-	-	-	-
di-n-octyl phthalate	OK34	-	≤40.0[6]	-	-	-	-	-11.8-162[7]	-	-	-	-	-	-	-
dibenz(a,h)anthracene	OK36	-	≤40.0[6]	-	-	-	-	-72-258[7]	-	-	-	-	-	-	-
dibenzofuran	OK38	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
diethyl phthalate	OK39	-	≤40.0[6]	-	-	-	-	-25.3-113[7]	-	-	-	-	-	-	-
dimethyl phthalate	OK40	-	≤40.0[6]	-	-	-	-	-42.4-84.5[7]	-	-	-	-	-	-	-
fluoranthene	OK45	-	≤40.0[6]	-	-	-	-	14.9-149[7]	-	-	-	-	-	-	-
fluorene	OK46	-	≤40.0[6]	-	-	-	-	53.1-127[7]	-	-	-	-	-	-	-
hexachlorobenzene	OK47	-	≤40.0[6]	-	-	-	-	-20.1-169[7]	-	-	-	-	-	-	-
hexachlorobutadiene	OK48	-	≤40.0[6]	-	-	-	-	13.9-126[7]	-	-	-	-	-	-	-
hexachlorocyclopentadiene	OK49	-	≤40.0[6]	-	-	-	-	25-125[4]	-	-	-	-	-	-	-
hexachloroethane	OK50	-	≤40.0[6]	-	-	-	-	33.0-111[7]	-	-	-	-	-	-	-
indeno(1,2,3-cd)pyrene	OL05	-	≤40.0[6]	-	-	-	-	-36.1-186[7]	-	-	-	-	-	-	-
isophorone	OL06	-	≤40.0[6]	-	-	-	-	0.35-226[7]	-	-	-	-	-	-	-
naphthalene	OL11	-	≤40.0[6]	-	-	-	-	9.80-145[7]	-	-	-	-	-	-	-
nitrobenzene	OL12	-	≤40.0[6]	-	-	-	-	19.5-192[7]	-	-	-	-	-	-	-
pentachlorophenol	OL18	≤25.8	≤34.1	9.01	8.37	-	36.4-125	14.3-147	80.63	22.11	-	45.4-120	26.9-138	82.55	18.55
phenanthrene	OL20	-	≤40.0[6]	-	-	-	-	47.1-127[7]	-	-	-	-	-	-	-
phenol	OL21	≤16.4	≤21.8	5.53	5.41	-	57.3-105	45.3-117	81.22	11.96	-	54.0-97.3	43.2-108	75.63	10.82
pyrene	OL24	≤20.1	≤26.8	6.83	6.65	-	57.4-119	42.0-134	88.10	15.36	-	53.6-118	37.6-133	85.55	15.98

Table 6
QC Limits (cont'd)
Page Twelve

QUALITY CONTROL TEST FILE
SEMIVOLATILE ORGANICS - GC/MS
SOIL
PM: E30% AM: 010S%

COMPOUND	COMBO	PRECISION AS RPD WL	CL	X	S	CPK[1]	PERCENT RECOVERY OF LAB CONTROL STANDARDS WL	CL	X	S	CPK[2]	PERCENT RECOVERY OF MATRIX SPIKES 95% CI	99% CI	X	S
2,4,6-tribromophenol (S)	OJ05	NA	NA	NA	NA	NA	36.8-99.7	21.1-115	68.28	15.73	-	NA	NA	NA	NA
2-fluorobiphenyl (S)	OJ16	NA	NA	NA	NA	NA	55.7-80.3	49.5-86.5	68.02	6.16	-	NA	NA	NA	NA
2-fluorophenol (S)	OJ17	NA	NA	NA	NA	NA	56.0-109	42.9-122	82.37	13.17	-	NA	NA	NA	NA
nitrobenzene-d5 (S)	OL13	NA	NA	NA	NA	NA	59.0-79.5	53.9-84.7	69.27	5.13	-	NA	NA	NA	NA
p-terphenyl-d14 (S)	OL16	NA	NA	NA	NA	NA	45.5-98.8	32.2-112	72.16	13.33	-	NA	NA	NA	NA
phenol-d5 (S)	OL22	NA	NA	NA	NA	NA	55.7-88.7	47.5-96.9	72.20	8.23	-	NA	NA	NA	NA

TABLE 7

ORGANIC EXTRACTION LAB SAMPLE DESCRIPTION NOTES			
#	CHARACTERISTICS	#	CHARACTERISTICS
	Color As Received	20	Oil smell
1	Milky white	21	Sulfur smell
2	Yellow	22	Vinegar smell
3	Orange	23	Fish smell
4	Pink		**Concentration**
5	Brown	31	Very volatile, concentrated fast
6	Black	32	Very foamy, concentrated slow
7	Blue	33	Bumps, splatters, boils sluggishly
8	Green	34	Stopped concentrating before appropriate volume
9	Red	35	Particulate fallout
10	Purple	36	Phase separation
11	Grey	37	Nitrogen Blowdown req.
12	Turned with add of NaOH		**Emulsion**
13	Turned with add of H_2SO_4	41	Slight-needed centrifugation
14	Clear	42	Moderate-needed centrifugation
15	Opaque	43	Dense-centrifugation not good
	Odor As Received		**pH**
16	Strong	46	Basic
17	Very strong	47	Acidic
18	Phenol smell	48	Buffered
19	Solvent smell (paint)	49	Over 5 mL NaOH
	pH (Continued)	62	Wood
50	Over 100 mL NaOH	63	Very Fine Dust
51	Over 5 mL H_2SO_4	64	Clay
52	Over 10 mL H_2SO_4	65	Tar
	Soil Consistency	66	Filtered slow
56	Rocks	67	Viscous
57	Very Moist		**TCLP**
58	Sludge	71	Routine
59	Vegetation	72	CLP
60	Carbon	73	Filter
61	Ropes		

FIGURE 1

Extraction Log

TITLE EASTLL LLS BNA EXAMPLE ONLY PROJECT NO. BOOK NO. 150-91 52

SAMPLE #	ALIQUOT	Na_2SO_4	FINAL VOL.	DESCRIPTION	DUPLICATE
P170943	30.02g	29.97g	1.0 mL	64	
P170945	30.60g	29.99g		64	
P170946	30.05g	30.05g		64	
P170947	29.97g	30.02g		64	
P170948	30.02g	29.97g		64	
P170949	30.01g	30.04g		64	
P170949 MS	29.97g	29.99g			
P170949 MSD	29.99g	30.01g			
P170950	30.01g	29.92g		64,50,57	
P170951	30.03g	29.96g			
P170955	29.99g	30.02g			
P170959	29.97g	30.04g		56,57	
BLANK					

1.0 mL BNA surrogate (1-37-91-107) added to all samples.
1.0 mL BNA spike (2-37-91-125) added to all 949 MS/MSD.
Batch No.: 1247
Extraction: 8/5/91 8:15am - 10:15 am Blank Analyst
Concentration: 8/5/91 2:10pm - 3:30 pm [illegible] / Stand Analyst
Final Concentration Method: Water Bath

SIGNATURE DATE

DISCLOSED TO AND UNDERSTOOD BY DATE WITNESS Frank Smith DATE 8/6/91

FIGURE 2

Semivolatiles Assignment Sheet

GCMS Assignment Sheet (29-Jul-92 Samples 206415 - 206416)

Due Date: ___-___-___ Date entered and init.: ___-___-___ _____
Approved and init.: ___-___-___ _____

Sample: F206415 Test: OSYPPV Type: ORIG Run File Dilution Log Page Anlst/Processor(Espf)
Analysis Number: 10 Anls. Ref. Number:
Analyst (Espf) Number: _____
Date Analyzed: ___-___-___ Time: _____
Instrument: GCMS _____
Book: _____-_____ Page: _____
Sample Description: S/G HAUSOLEUM SLRRY / TCLP LEACH Time Sampled: Received Original (vol/wt): _____
Client: 17-JUL-92 Final (vol): _____
UNITS: _____ BLANK SAMPLE #: _____ RUN BATCH #: _____ Prep Meth: E290ABNAE- Anls Meth: C10ABNAE-
CASE ID: Not Available SDG: Not Available

SEMIVOLATILE EXTRACTABLES

ANALYTE	DETECTION LIMIT	RESULT	QUALIFIER
1,2,4-Trichlorobenzene			
1,2-Dichlorobenzene			
1,2-Diphenylhydrazine (as Azobenzene)			
1,3-Dichlorobenzene			
1,4-Dichlorobenzene			
2,4,6-Trichlorophenol			
2,4-Dichlorophenol			
2,4-Dimethylphenol			
2,4-Dinitrophenol			
2,4-Dinitrotoluene			
2,6-Dinitrotoluene			
2-Chloronaphthalene			
2-Chlorophenol			
2-Nitrophenol			
3,3'-Dichlorobenzidine			
4,6-Dinitro-o-cresol			
4-Bromophenylphenylether			
4-Chlorophenylphenylether			
4-Nitrophenol			
Acenaphthene			
Acenaphthylene			
Anthracene			
Benzidine			
Benzo(a)anthracene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(g,h,i)perylene			
Benzo(k)fluoranthene			
Butylbenzylphthalate			
Chrysene			
Di-n-butylphthalate			
Di-n-octylphthalate			
Dibenzo(a,h)anthracene			
Diethylphthalate			
Dimethylphthalate			
Fluoranthene			
Fluorene			

EXAMPLE ONLY

FIGURE 2 (CONT'D)

GCMS Assignment Sheet (29-Jul-92 Samples 206415 - 206416)

ANALYTE	DETECTION LIMIT	RESULT	QUALIFIER
Hexachlorobenzene			
Hexachlorobutadiene			
Hexachlorocyclopentadiene			
Hexachloroethane			
Indeno(1,2,3-cd)pyrene			
Isophorone			
N-Nitrosodi-n-propylamine			
N-Nitrosodimethylamine			
N-Nitrosodiphenylamine			
Naphthalene			
Nitrobenzene			
Pentachlorophenol			
Phenanthrene			
Phenol			
Pyrene			
bis(2-Chloroethoxy)methane			
bis(2-Chloroethyl)ether			
bis(2-Chloroisopropyl)ether			
bis(2-Ethylhexyl)phthalate			
p-Chloro-m-cresol			
SURROGATES			
2,4,6-Tribromophenol			
2-Fluorobiphenyl			
2-Fluorophenol			
Nitrobenzene-d5			
Phenol-d5			
p-Terphenyl-d14			

EXAMPLE ONLY

COMMENTS: _____

Special Instructions

P206415 TYPE C

FIGURE 3

GC/MS Injection Log

Halliburton NUS Laboratory Services Group

Semivolatile Organic GC/MS Analysis Notebook #:

Date:

Client:

PARAMETERS		He flow:	STANDARDS:
Column:		Col. head pressure:	dftpp:
Prog:		(inj. @):	bna:
Source temp:	EM:	Cylinder Pressures:	
Trans. temp:	Em.curr:	He carrier:	
Inj. temp:	L3:	air:	
Sep. temp:	L4:		
Initial Cali:	L5:	Quad off:	Temp. tape:

Run#	File name	Ident	Dilution	Libr	Comments	Perm Tape

EXAMPLE ONLY

Comments:

Analyst :

Date:

Reviewer:

Date:

Halliburton NUS
CORPORATION

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Pittsburgh, Pennsylvania 15205

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FAX: (412) 747-2559

LABORATORY METHOD

ORGANOCHLORINE PESTICIDES/PCBs ANALYSIS BY GAS CHROMATOGRAPHY

METHOD ID: CRA/SN-PEST
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

ORGANOCHLORINE PESTICIDES/PCBs ANALYSIS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

This method covers the determination of priority pollutant and US EPA CLP Target Compound List (TCL) organic pesticides and polychlorinated biphenyls (PCBs) in water and soil/sediment. Reporting limits are listed in Table 1 for TCL and priority pollutant analyses and Table for residential well analyses.

2.0 SUMMARY OF METHOD

Water samples are prepared for analysis by liquid-liquid solvent extraction. Procedures for continuous and separatory funnel extractions are provided. Soil/sediment samples are prepared for analysis by sonication. A low level extraction using 30 grams of sample is used routinely. However, for samples containing more than 20 mg/kg semivolatile and nonvolatile organics, a medium level extraction procedure using 1 gram of sample is used.

Hexane extracts are analyzed by gas chromatography (GC) using an electron capture detector (ECD). Quantitation is accomplished using a wide bore capillary column (ID >0.32 mm). The presence of pesticides or PCBs is confirmed by a second GC/ECD analysis on a fused-silica capillary column.

3.0 EXTRACTION PROCEDURES

3.1 SAMPLE PRESERVATION

3.1.1 Water Samples

Water samples are stored at 1 - 5 degrees C. Extraction must be completed within 7 days of sampling. If sample pH is <5 or >9, extraction must be completed within 72 hours of sampling.

Approvals:

Technical Operations Manager	4/12/94 Date	Quality Assurance Director	4/12/94 Date	Group Leader	4/1 Date

3.1.2 Soil/Sediment Samples

Soil/sediment samples are stored at 1 - 5 degrees C. Extraction must be completed within 14 days of sampling.

3.2 CONTINUOUS LIQUID-LIQUID EXTRACTION OF AQUEOUS SAMPLES

3.2.1 Set up the extraction equipment in an operating fume hood.

3.2.2 Close the extractor body stopcock.

3.2.3 Add approximately 300 mL of methylene chloride measured in a 500-mL graduated cylinder to the extractor body. Add approximately 300 mL of methylene chloride and several boiling chips to a 1000-mL round-bottom flask.

3.2.4 Shake the sample container to mix the contents thoroughly. Measure 1 liter of sample in a glass 1-liter graduated cylinder.

3.2.5 Transfer the 1 liter sample to the extractor body.

3.2.6 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of the surrogate standard spiking solution into each sample in the extractor and mix well.
- Prepare a lab control standard (LCS) by spiking the indicated volume of the LCS/matrix spiking solution into 1 liter of reagent water with each batch of samples extracted.
- For samples selected for matrix spiking, add the indicated volume of the matrix spiking standard and mix well.

3.2.7 Assemble the extraction equipment as follows:

3.2.7.1 Insert the condenser into the top of the extractor body.

3.2.7.2 Maintain the extractor body in an upright position using a large clamp attached to a ring stand or similar support.

3.2.7.3 Attach the round-bottom flask to the side-arm of the extractor body.

3.2.7.4 Place the round-bottom flask in a heating mantle.

3.2.7.5 Use Teflon tape to seal all the joints.

3.2.8 Extract the sample as follows:

3.2.8.1 Open the extractor body stopcock.

3.2.8.2 Turn on the water supply to the condenser.

The water pressure should be sufficient to cycle the water in the condenser, but should not force off any tubing connections from the water supply to the condenser.

3.2.8.3 Turn on the heating mantle and adjust the temperature setting to "7".

3.2.8.4 Extract the sample for 18-24 hours.

3.2.8.5 Check the extractor body/condenser periodically during the extraction process for the following:

- A drip rate of approximately 1-2 drops/second from the bottom of the condenser into the extractor body.
- Approximately 1/4 to 1/3 of the bottom of the condenser should be wet from the extract if the distillation is proceeding at the proper temperature.

Adjust the heating mantle temperature setting as necessary to achieve these conditions.

3.2.9 Turn off the power to the heating mantle when the extraction is complete. Allow the flask to cool for approximately 1.5 hours before removing it from the extractor body.

3.2.10 Prepare a drying column containing anhydrous sodium sulfate. See Section 9.1.2 for instructions on column preparation. Set up the drying column using a clamp attached to a ring stand.

Connect a 500-mL Kuderna-Danish (K-D) evaporation flask to a 10-mL concentrator tube. Place the K-D apparatus beneath the column to collect the extract.

3.2.11 Close the extractor body stopcock. Remove the flask containing the solvent extract and carefully pour the extract through the column. Collect the dried extract in the K-D apparatus. If the sodium sulfate hardens at any point during the drying process:

3.2.11.1 Break up the hardened mass, if possible, with a pipet and add 20-30 mL of elution solvent to the column to rinse it.

3.2.11.2 Start a new drying column, if necessary, to pass through any remaining solvent extract.

3.2.11.3 Repeat these steps as necessary until all the solvent fractions have been passed through drying columns into the collection device.

3.2.12 Rinse the flask that contained the extract with 10 - 20 ml of methylene chloride and add it to the drying column to complete a quantitative transfer.

3.2.13 Concentrate the extract as follows:

3.2.13.1 Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

3.2.13.2 Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

3.2.13.3 Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

3.2.13.4 Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

3.2.13.5 Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.2.14 Momentarily remove the Snyder column, add 50 mL of hexane, and reattach the Snyder column. Mix the extract by swirling.

3.2.15 Repeat step 3.2.13. Raise the temperature of the water bath, if necessary, to maintain proper distillation.

3.2.16 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of hexane.

3.2.17 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.3 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION OF AQUEOUS SAMPLES

3.3.1 Set up the extraction equipment in an operating fume hood. Put the separatory funnel, with the Teflon stopcock closed, into a large metal ring attached to a ring stand.

3.3.2 Shake the sample container to mix the contents thoroughly. Measure 1 liter of sample in a glass graduated cylinder and transfer it quickly to the separatory funnel. Stopper the funnel.

3.3.3 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of the surrogate standard spiking solution into each sample in the funnel and mix well.
- Prepare a lab control standard (LCS) by spiking the indicated volume of the LCS/matrix spiking solution into 1 liter of reagent water with each batch of samples extracted.
- For samples selected for matrix spiking add the indicated volume of the matrix spiking standard and mix well.

3.3.4 Add approximately 60 mL of methylene chloride measured in a 100-mL graduated cylinder to the separatory funnel.

3.3.5 Seal the separatory funnel. Invert <u>once</u> and vent the funnel into the hood by opening the stopcock. While the stopcock is still open, swirl the contents of the flask to mix well.

Note: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted once.

Close the stopcock. Shake the inverted funnel vigorously for 1-2 min. with periodic venting through the stopcock to release excess pressure.

3.3.6 Replace the funnel in the ring stand. Allow the organic layer to separate from the water phase for a minimum of 10 minutes.

If the emulsion interface between layers is more than one-third the size of the solvent layer, use mechanical techniques to complete the phase separation. The best technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Consult with the Group Leader, if required, to determine the best method for optimum separation. Document such measures in the extraction log.

3.3.7 Prepare a drying column containing anhydrous sodium sulfate. See Section 9.1.2 for instructions on column preparation. Set up the drying column near the separatory funnel using a clamp attached to the ring stand.

Connect a 500-mL Kuderna-Danish (K-D) evaporation flask to a 10-mL concentrator tube. Place the K-D apparatus beneath the column to collect the extract.

3.3.8 Hold the separatory funnel over the drying column and open the stopcock to remove the solvent fraction. Dry the extract by passing it through the drying column. Collect the dried extract in the K-D apparatus. If the sodium sulfate hardens at any point during the drying process:

3.3.8.1 Break up the hardened mass, if possible, with a pipet and add 20-30 mL of elution solvent to the column to rinse it.

3.3.8.2 Start a new drying column, if necessary, to pass through any remaining solvent extract.

3.3.8.3 Repeat these steps as necessary until all the solvent fractions have been passed through drying columns into the collection device.

3.3.9 Repeat the solvent extraction two more times using fresh portions of solvent (steps 3.3.4 through 3.3.8). Collect the three solvent extracts in the same K-D apparatus.

Following the final extraction, add 20-30 mL of methylene chloride to the column to complete the quantitative transfer.

3.3.10 Concentrate the extract as follows:

3.3.10.1 Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

3.3.10.2 Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

3.3.10.3 Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

3.3.10.4 Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

3.3.10.5 Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.3.11 Momentarily remove the Snyder column, add 50 mL of hexane, and reattach the Syder column. Mix the extract by swirling.

3.3.12 Repeat step 3.2.10. Raise the temperature of the water bath, if necessary, to maintain proper distillation.

3.3.13 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of hexane.

3.3.14 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.4 SONICATION EXTRACTION OF IN SOIL/SEDIMENT

3.4.1 Sample Preparation

Decant and discard any water layer. Discard foreign objects such as sticks, vegetation, and rocks. Mix the sample thoroughly, especially composited samples.

3.4.2 Low Level Soil Extraction and Initial Concentration

3.4.2.1 Tune the sonicator as described in Table 4 to check its operation.

3.4.2.2 Aliquot the samples as follows. Perform these steps rapidly to avoid loss of the more volatile extractables:

a. Place a 400-mL glass beaker on the weighing pan of a balance and tare the balance.

b. Mix the sample thoroughly with a spatula and transfer approximately 30 grams of sample to the beaker. Record the weight to the nearest 0.01 gram.

c. Mix nonporous or wet samples (i.e., gummy or clay type samples) that do not have a free-flowing and/or sandy texture with anhydrous sodium sulfate to dry them as follows:

- Tare the balance holding the sample beaker.
- Add approximately 30 grams of anhydrous sodium sulfate to the beaker. Record the weight to the nearest 0.01 gram.
- Mix thoroughly using a spatula. Check if the texture appears free-flowing and/or sandy.
- Add additional anhydrous sodium sulfate in 30 gram increments (approx.) as necessary until the sample consistency is free-flowing and/or sandy.
- Record the total amount of sodium sulfate to the nearest 0.01 gram.

3.4.2.3 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of surrogate standard spiking solution onto each sample in the beaker.
- Prepare a lab control standard (LCS) by spiking the indicated volume of the LCS/matrix spiking solution onto 30 grams of clean sand with each batch of samples extracted.
- For samples selected for matrix spiking add the indicated volume of the matrix spiking standard.

3.4.2.4 Immediately add approximately 100 mL of 1:1 (v:v) methylene chloride:acetone measured in a glass graduated cylinder.

3.4.2.5 Sonicate the sample as follows:

a. Attach the ¾-inch disrupter horn (No. 207) to a heavy-duty ring stand using a large vinyl-coated clamp. See Section 9.1.7 for additional information on the equipment.

b. Place the tip of the disrupter horn about ½-inch below the surface of the solvent but above the sediment layer.

c. Sonicate for 3 minutes with the output control knob set at 8 to 10, the mode switch on "Pulse" and the percent-duty cycle knob set at 20%.

- The solvent layer should be "churning" but not overflowing the sides of the beaker.
- Do not touch the tip of the disrupter horn to the sides or bottom of the beaker because damage to the horn or beaker may occur.

3.4.2.6 Decant the extract through Whatman No. 41 filter paper lining a glass funnel. Collect the extract in a 10-mL Kuderna-Danish (K-D) concentrator tube attached to a 500-mL evaporation flask.

3.4.2.7 Repeat the sonication two more times with additional 100 mL portions of solvent. Decant and filter the solvent phase after each sonication.

On the final filtration, transfer the entire sample into the funnel. Rinse the beaker with approximately 20-30 mL of solvent to complete the quantitative transfer.

3.4.2.8 Concentrate the extract as follows:

a. Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

b. Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

c. Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

d. Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

e. Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.4.2.9 Momentarily remove the Snyder column, add 50 mL of hexane, and reattach the Syder column. Mix the extract by swirling.

3.4.2.10 Repeat step 3.4.2.8. Raise the temperature of the water bath, if necessary, to maintain proper distillation.

3.4.2.11 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of hexane.

3.4.2.12 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.4.3 Medium Level Soil Extraction and Initial Concentration

3.4.3.1 Tune the sonicator as described in Table 4 to check its operation.

3.4.3.2 Aliquot the samples as follows. Perform these steps rapidly to avoid loss of the more volatile extractables:

a. Place a 10-mL glass scintillation vial on the weighing pan of a balance and tare the balance.

b. Mix the sample thoroughly with a spatula and transfer approximately 1 gram of sample to the vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the weight to the nearest 0.01 gram.

c. Mix nonporous or wet samples (i.e., gummy or clay type samples) that do not have a free-flowing and/or sandy texture with anhydrous sodium sulfate to dry them as follows:

- Tare the balance holding the sample vial.
- Add approximately 1 gram of anhydrous sodium sulfate to the vial. Record the weight to the nearest 0.01 gram.

- Mix thoroughly using a spatula. Check if the texture appears free-flowing and/or sandy.
- Add additional anhydrous sodium sulfate in 1 gram increments (approx.) as necessary until the sample consistency is free-flowing and/or sandy.
- Record the total amount of sodium sulfate to the nearest 0.01 gram.

3.4.3.3 Use a glass volumetric pipet to spike the samples as follows. See Table 3 for spiking compounds/concentrations/volumes and Section 6.0 for quality control frequency and corrective action requirements.

- Pipet the indicated volume of surrogate standard spiking solution onto each sample in the vial.
- Prepare a lab control standard (LCS) by spiking the indicated volume of LCS/matrix spiking solution onto 1 gram of clean sand with each batch of samples extracted.
- For samples selected for matrix spiking add the indicated volume of matrix spiking standard.

3.4.3.4 Immediately add enough 1:1 (v:v) methylene chloride:acetone to bring the final volume to 10.0 mL including the surrogate and/or matrix spike volumes.

3.4.3.5 Sonicate the sample as follows:

a. Attach the 1/8-inch microtip ultrasonic probe (No. 419) to a heavy-duty ring stand using a large vinyl-coated clamp. See Section 9.1.17 for additional information on the equipment.

b. Place the tip of the probe below the surface of the solvent but above the sediment layer.

c. Sonicate for approximately 3 minutes with the output control knob set at 4 to 5, the mode switch on "Pulse" and the percent-duty cycle knob set at 20%.

- The solvent layer should be "churning" but not overflowing the sides of the vial.

- Do not touch the tip of the probe to the sides or bottom of the vial because damage to the horn or vial may occur.

3.4.3.6 Filter the extract as follows:

a. Loosely pack a Pasteur pipet with a small plug of clean glass wool. See Section 9.1.2 for detailed instructions on pipet preparation.

b. Using a small clamp attached to a ring stand, support the filtering pipet in an upright position over a 10 mL Kuderna-Danish (K-D) concentrator tube.

c. Use a separate pipet to transfer the extract from the vial to the filtration apparatus.

d. Collect the extract to the 5 mL mark of the concentrator tube by gravity filtration through the glass wool.

3.4.3.7 Concentrate the extract as follows:

a. Add several clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column with a Pasteur pipet.

b. Place the K-D apparatus on a hot water bath (80-90°C or "HIGH" setting) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor.

c. Adjust the vertical position of the equipment and the water temperature as required to complete the concentration in 10-20 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

d. Check the remaining volume periodically. Allow the extract to concentrate until the volume reaches the 1 mL mark on the concentrator tube.

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

e. Remove the equipment from the water bath and allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

3.4.3.8 Momentarily remove the Snyder column, add 50 mL of hexane, and reattach the Syder column. Mix the extract by swirling.

3.4.3.9 Repeat step 3.4.3.8. Raise the temperature of the water bath, if necessary, to maintain proper distillation.

3.4.3.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of hexane.

3.4.3.11 Proceed to Section 3.5 for instructions on final concentration of the extract.

3.5 FINAL EXTRACT CONCENTRATION

Note: Final concentration of the extract is completed by the micro Snyder technique described below (step 3.6.1) or the nitrogen blowdown technique (step 3.6.2).

3.5.1 Concentrate the extract as follows:

3.5.1.1 Add one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of solvent to the top of the column.

3.5.1.2 Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Swirl the tube in the water if necessary to begin the distillation process.

3.5.1.3 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 min.

At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood.

3.5.1.4 When the apparent volume of liquid reaches approximately 0.5 mL, remove the K-D apparatus from the water bath. Allow it to drain until the tube feels cooled to room temperature by touch (approx. 10 minutes).

Do not allow the concentrator tube to become dry. If this occurs, repeat the extraction.

3.5.1.5 Remove the Snyder column. Adjust the final volume to 10.0 mL with hexane.

3.5.2 An alternate procedure to step 3.6.1 is the nitrogen blowdown technique as described below:

3.5.2.1 Place the concentrator tube in the heating block set at 30-35°C. Evaporate the solvent to 0.5-0.8 mL using a gentle stream of clean, dry nitrogen gas dispensed through a Luer-Lock blunt tip needle.

Do not allow the extract to become dry. If this occurs, repeat the extraction.

Use a clean, dry Luer-Lock blunt tip needle for each sample.

3.5.2.2 Adjust the final volume to 10.0 mL with hexane.

3.5.3 Transfer the extract to a Teflon-sealed, screw-cap vial labeled with the sample number, fraction, and extraction date.

4.0 GC ANALYSIS

4.1 EXTRACT PRESERVATION

Store extracts at 1 - 5 degrees C. Complete analysis within 40 days of extraction.

4.2 PREPARATION OF STANDARDS

Stock standards are purchased commercially in sealed ampoules. Depending on the concentration of the purchased solution, intermediate or working standards are prepared in hexane chloride. Aliquots of stock solutions are combined as necessary to prepare intermediate or working standards that contain the analytes of interest. Prepare standard solutions as follows.

4.2.1 Check the expiration date on any stock or intermediate standard to be diluted. Discard material exceeding the expiration date according to waste management procedures.

4.2.2 Determine the appropriate volume of standard material to add to the flask to obtain the desired final concentration as follows:

$$V = (DC/SC) \times FV$$

where V = volume of standard material to be added

DC = desired concentration
SC = standard material concentration
FV = final volume

4.2.3 Fill a volumetric flask just to the neck with dilution solvent.

4.2.4 Using a syringe, quickly transfer the appropriate amount of standard to the flask to obtain the desired concentration in µg/mL. Use a syringe to add the liquid material directly to the solvent without contacting the neck of the flask. Immerse the needle tip below the surface of the solvent before expelling the solution to reduce evaporation of the standard material.

4.2.5 Add dilution solvent until the bottom of the meniscus reaches the volume mark of the flask using a disposable pipet. Place the tip of the pipet close to the volume mark without immersing it in the dilution solvent. Avoid wetting the neck of the flask above the volume mark.

4.2.6 Stopper the flask and invert three times to mix thoroughly.

4.2.7 Transfer aliquots of intermediate standard solutions to 2-mL vials without headspace using a Pasteur pipet. Label bottles or vials containing standard solutions with the following information:

- Solution name and concentration - use sufficient detail in the description to identify it from other solutions.
- Identification number.
- Date prepared and preparer.
- Expiration date.

4.2.8 Store volatile and semivolatile standard solutions in separate refrigerated storage areas to prevent cross-contamination of standard materials and/or solvents. Store standard solutions in Teflon-sealed containers at $\leq$ 4° C.

Mark the meniscus level on any container where headspace in the vial is apparent.

4.2.9 Visually check standard stock solutions prior to use for evidence of degradation or evaporation. Replace the solutions every six months, or sooner if degradation or evaporation occurs or if comparison with quality control check samples indicate a problem.

4.3 ANALYSIS SEQUENCE

4.3.1 **GC Operating Conditions**

Set the GC operating conditions as shown in Table 5 and allow the system to stabilize.

4.3.2 **Solvent Blank**

Run a hexane blank. The baseline must be flat, with no peaks at or above the reporting limit of target analytes prior to proceeding with analysis.

4.3.3 **Breakdown Check**

Run a breakdown check before each initial or continuing calibration. The breakdown check consists of 0.01 µg/mL of 4,4'-DDT and 0.02 µg/mL of Endrin in hexane.

4.3.3.1 Calculate the percent breakdown (%B) of Endrin and DDT as follows:

$$\%B_{Endrin} = \frac{\text{peak area (aldehyde + ketone)}}{\text{peak area (Endrin + aldehyde + ketone)}} \times 100$$

$$\%B_{DDT} = \frac{\text{peak area (DDE + DDD)}}{\text{peak area (DDT + DDE + DDD)}} \times 100$$

4.3.3.2 Meet the following criteria for the breakdown check before proceeding with analysis:

- $\%B_{DDT} \leq 20\%$
- $\%B_{Endrin} \leq 20\%$
- $\%B_{DDT} + \%B_{Endrin} \leq 30\%$

4.3.3.3 If the criteria are not met, take corrective action as follows:

- Packed column - replace the dimister trap if off-column injection is used and/or change the glass wool in front of the column. Remove the first few mm of packing material if any discoloration is noted. Swab out the inside walls of the column if residue is observed. If this does not eliminate the problem, repack the column.
- Capillary column - clean and deactivate the glass injection port insert or replace it with a clean, deactivated insert.

Break off the first few inches to one foot of injecting port side of column. Flush column with solvent according to the manufacturer's instructions. If this does not eliminate the problem, replace the column.

- Silynize the injection port.

4.3.4 **Initial Calibration**

Run an initial calibration prior to sample analysis and whenever continuing calibration criteria are not met. An initial calibration consists of the solvent blank, each single response target compound run at 5 concentration levels (see Table 6), and each multiresponse target compound run at a midpoint concentration.

Determine the correlation coefficient (r) of the solvent blank and 5 standard concentrations calibration. If $r \geq 0.995$, quantitate from the best-fit line. If $r < 0.995$, quantitate from the best-fit second order equation.

For single response pesticides, the linear range is defined as the concentration of the highest standard. Concentrations above this must be diluted into the linear range.

For multi-response compounds, the linear range is defined as two times the response of the mid-point calibration standard. Concentrations above this must be diluted into the linear range.

At the conclusion of a successful initial calibration, the 24-hour analysis sequence begins.

4.3.5 **Continuing Calibration**

Run a mid-point continuing calibration standard after 24 hours of sample analysis following completion of the initial calibration or the most recent continuing calibration, or at the start of a set of analyses.

Run standards for all target analytes in every run. If the samples are split between 2 or more instruments, analyze the complete set of standards on each instrument.

Acceptance limits for recovery are 85-115% for all target analytes. If acceptance limits are not obtained, evaluate the system for problems and run a new initial calibration.

4.3.6 **Sample Analysis**

Evaluate each injection for the following:

4.3.6.1 Evaluate the retention time shift of each surrogate. The shift must not exceed 2% for packed columns, 1.5% for wide bore capillary columns (I.D. >0.32 mm) or 0.3% for narrow bore capillary columns (I.D. $\leq$0.32 mm).

Calculate retention time shift (RTS) as follows:

$$\% D_{RTS} = \frac{RT_i - RT_e}{RT_i} \times 100$$

where:

RT_i = absolute retention time in the midpoint initial calibration standard or the continuing calibration standard, whichever was run at the start of the 24-hour sequence.

RT_e = absolute retention time in the sample.

4.3.6.2 Identify target analytes when the retention time of a peak falls within the retention time window of a standard analyzed within the same run. The daily retention time window uses the absolute retention time from the midpoint initial calibration or continuing calibration standard as the midpoint, and the retention time window as the range.

The identification of pesticide/PCB compounds may be confirmed by analysis on a second column at client request.

4.3.6.3 Determine if any target pesticide/PCB compounds are present at reportable quantities in the chromatograms using the following criteria:

- Report compounds as less than the reporting limit when the concentration is less than the reporting limits listed in Table 1 for TCL and priority pollutant analyses and Table 2 for residential well analyses.

- If the response for any of these compounds is at or above the reporting limit and within linear range (i.e., less than the highest initial calibration standard for single response compounds or less than 2 times the area of the initial calibration standard for multi-response compounds), quantitate these compounds from the run (see Section 4.5 below).

- If the response for any compound is outside the linear range, dilute the extract so that the peak will be:

  - between 25-100% of the highest calibration standard for single response compounds, and

  - between 50-200% of the one-point calibration for multi-response standards.

  Use this dilution for quantitation of these compounds.

  Note: If a dilution is required for analysis of a matrix spike, the unspiked sample and the duplicate spike must also be analyzed at the same dilution.

4.3.6.4 When a dilution of >10 fold is required, also inject an aliquot of a dilution 10 fold more concentrated to determine if other compounds of interest are present at lower concentrations.

Computer reproductions of chromatograms, manipulated to ensure all peaks are on scale over a 100 fold range, are an accepted substitute. However, this can be no greater than a 100 fold range to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100 fold range using higher concentrations of the evaluation mixture.

4.4 GC CONFIRMATION

4.4.1 Perform GC confirmation analysis for those compounds tentatively identified on the primary column only.

4.4.2 Select a column for confirmation which will provide $\leq 25\%$ resolution between peaks, which were identified by primary analysis.

4.4.3 Adhere to all QC measures specified for primary analysis in Section 6.0.

4.4.4 Use the same dilution for confirmation as was used for primary analysis.

4.4.5 Report a compound as confirmed if the retention time falls within the retention time window of a corresponding standard chromatographed within the analysis period.

4.5 QUANTITATION

4.5.1 Perform quantitation on either the primary or confirmatory column chromatogram if confirmation was performed. Use the best-fit line from the initial calibration if an initial calibration was run immediately before the samples. Otherwise, quantitate from the response factor (area/conc.) of the continuing calibration standard.

4.5.2 Calculate the concentration of target compounds and the surrogate using the following equations.

For multiresponse compounds (chlordane, toxaphene and PCBs), quantitate every identifiable peak (>50% of the total area must be used) unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

4.5.2.1 **Quantitation from Initial Calibration**

$$\text{Water: } \mu g/L = \frac{A_x - b}{m} \times \frac{V_o}{V_s} \times \frac{DFV}{DIV}$$

$$\text{Soil: } \mu g/kg = \frac{A_x - b}{m} \times \frac{V_o}{W_s} \times \frac{1000\ g}{kg} \times \frac{DFV}{DIV}$$

4.5.2.2 **Quantitation from Continuing Calibration**

$$\text{Water: } \mu g/L = A_x \times \frac{C_s}{A_s} \times \frac{V_o}{V_s} \times \frac{DFV}{DIV}$$

$$\text{Soil: } \mu g/kg = A_x \times \frac{C_s}{A_s} \times \frac{V_o}{W_s} \times \frac{1000\ g}{kg} \times \frac{DFV}{DIV}$$

where:

A_x = Response for the parameter to be measured
A_s = Response for the external standard
V_o = Volume of total extract (mL)
W_s = Weight of sample extracted (g)
V_s = Volume of water extracted (L)

C_s = Concentration of the calibration standard
b = y-intercept of best-fit line
m = Slope of best-fit line
DIV = Dilution initial volume (1 if no dilution)
DFV = Dilution final volume (1 if no dilution)

Note: Because weathering and/or different formulations of chlordane usually modify the pattern exhibited by

technical chlordane, this method is not appropriate for determining technical chlordane. Instead, standards for alpha chlordane and gamma chlordane are used for quantitation, and each isomer of chlordane is reported separately.

4.5.3 Report results in µg/L or µg/kg without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

5.0 DATA COLLECTION

5.1 EXTRACTION

Document the following in a bound lab notebook for each set of extractions performed. Entries must be made at the time of extraction and concentration. An example logbook entry is shown in Figure 1 and briefly described below:

- preparation method code (root code) and brief description (e.g., LLW PPCBs).
- date and time extraction started and completed, and analyst(s) signature(s).
- date and time concentration started and completed, and analyst(s) signature(s).
- method of final concentration (water bath or nitrogen blowdown technique).
- lab sample number, sample aliquot, and descriptive codes (see Table 7) for each sample. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added.

Forward the following to data management from each set of extractions for data package preparation:

- description of problems encountered and actions taken during sample analysis on corrective action records.
- logbook page(s).

5.2 ANALYSIS

Document all data in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. Examples of appropriate forms for data collection (i.e., assignment sheets and injection log) are shown on Figures 2 and 3.

Data collection should include the following:

- brief description of the test (e.g., PPCB).
- date analysis started and analyst(s) signature(s).
- lab sample number and aliquot, and data system filename. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added.

Forward the following to data management from run for data package preparation:

- description of problems encountered and actions taken during sample analysis on corrective action records.
- initial and continuing calibration files.
- sample and associated quality control sample files (method blank, lab control standard, MS/MSD).
- Chromatograms and quantitation reports for samples and associated quality control samples.
- logbook page(s) and assignment sheets.

6.0 QUALITY CONTROL

6.1 SOLVENT PRESCREEN

Prescreen each lot of solvent prior to use as described in NUS Laboratory Procedure AP-001, Reagent Screening Program. Use only approved lots of solvent in sample extraction.

6.2 RETENTION TIME WINDOWS

Calculate retention time windows for each target pesticide/PCB for each column type.

Establish a new retention time window (RTW) whenever a new type of GC column is installed or operating conditions are modified.

Use the following guidelines in establishing RTWs:

6.2.1 The GC operating conditions must be adjusted such that 4,4'-DDT has a retention time $\geq$12 minutes on packed GC columns.

6.2.2 Three injections of all single component mixtures and multiresponse pesticide/PCB must be made over a 72-hour period.

6.2.3 The retention time shift as % difference for the surrogates in each standard must be:

- <2% for packed columns
- <0.3% for capillary columns (I.D. <0.32 mm)
- <1.5% for wide bore capillary columns (I.D. >0.32 mm)

6.3 COLUMN EVALUATION

Analyze the breakdown check at the beginning of each analysis sequence. The percent breakdown (%B) of 4,4'-DDT and endrin must be $\leq$20% each, and the combined breakdown $\leq$30%. If %B criteria is exceeded, take corrective measures before analysis proceeds.

6.4 INITIAL AND CONTINUING CALIBRATION

Analyze all single response compounds at 5 concentration levels and evaluate linearity as described in Section 4.3.4. Analyze all multi-response compounds at a mid-level concentration.

After 24 hours of sample analysis and at the start of a new set of analyses, run a mid-point continuing calibration standard. For all single response target analytes, the standard must recover within 15% when compared to the initial calibration.

6.5 METHOD BLANKS

Method blanks must be prepared and analyzed with each batch of up to twenty samples of similar concentration and matrix extracted together.

Analyze and evaluate the method blanks as described in Section 4.3.6 concurrently with the samples from the batch. Each blank must meet the following additional criteria:

- The method blank must contain less than the reporting limit of all target compounds.

- The surrogate spike recoveries of the method blank must be within the limits listed on Table 8. If they are not, take corrective measures before sample analysis proceeds, which may include verification of the spiking solution.

6.6 LAB CONTROL STANDARD (LCS)

An LCS must be prepared and analyzed with each batch of up to twenty samples of similar concentration and matrix extracted together.

Analyze and evaluate an LCS as described in Section 4.3.6 concurrently with the samples from the batch. Each LCS must meet the following criteria: recovery of at least 13 of the 14 LCS compounds the surrogate standard compounds must meet the must meet the limits listed in Table 8. If the recovery of 2 or more LCS compounds is unacceptable, troubleshoot the GC system, extraction, and/or standards. Re-extract the associated samples.

6.7 SURROGATE STANDARDS

Calculate the tetrachloro-m-xylene and decachlorophenyl spike recovery of each standard sample, blank, matrix spike, and matrix spike duplicate to monitor both sample preparation and analysis.

Re-extract samples with surrogate recoveries outside the control limits listed on Table 8. If surrogate spike recoveries comply after re-extraction then report the re-extraction results. Assume matrix interference if surrogate spike recovery limits remain out of conformance with QC test file limits after re-extraction. Report the original extract results with a qualification.

Calculate the retention time shift for decachlorophenyl and tetrachloro-m-xylene in all samples, standards, blanks, and MS/MSDs. The shift may not exceed the following:

- $<2\%$ on packed GC columns
- $<0.3\%$ on capillary columns
- $<1.5\%$ on wide bore capillary columns

6.8 MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

An MS/MSD must be prepared and analyzed with every twenty project samples of similar matrix and concentration.

When a sample requiring dilution has been chosen as the MS/MSD, the MS/MSD must be analyzed at the same dilution as the unspiked sample.

Calculate percent recovery as follows:

$$\text{Percent Recovery} = \frac{SSR - SR}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Calculate the relative % difference (RPD) as follows:

$$RPD = \frac{2(D_1 - D_2)}{(D_1 + D_2)} \times 100$$

where D_1 = MS Result
D_2 = MSD Result

Advisory MS/MSD percent recovery and RPD limits are listed on Table 8. Since these limits are for advisory purposes only, they should not be used to determine if sample reanalysis is required.

6.9 METHOD DETECTION LIMIT (MDL) STUDIES

A method detection limit study is performed for water analysis annually according to the procedure in 40 CFR 136, Appendix B. The statistically-based MDLs obtained from the study must be less than or equal to the reporting limits for the method.

6.10 CONTROL LIMITS

The statistically-based limits for precision and accuracy listed in Table 8 are updated periodically and, therefore, are subject to change.

7.0 INTERFERENCES

7.1 Solvents, reagents, glassware, and other sample processing hardware may be sources of contamination and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Use of specific "pesticide" grades of reagents is required.

7.2 Interferences coextracted from the sample matrix will vary considerably from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to cleanup procedures.

7.3 Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

8.0 SAFETY PRECAUTIONS

8.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

8.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

8.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

8.2 Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDS).

8.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

8.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

8.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

8.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

8.4 Handle all glass equipment with care, particularly during assembly and disassembly.

8.5 Vent each GC to the outside or through activated carbon.

9.0 APPARATUS AND MATERIALS

9.1 EXTRACTION

9.1.1 Continuous liquid-liquid extractor: Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Corning "One-Step", or equivalent).

9.1.2 Drying column: 20-mm I.D. Pyrex chromatographic column. If so equipped, the stopcock material should be Teflon. Use columns without frits.

Transfer a small pad of Pyrex glass wool to the bottom of the column by tamping with a glass stirring rod or pipet. The glass wool retains the adsorbent in the column.

Pack the column with approximately 10 cm (about 3 inches) of anhydrous sodium sulfate. Put a funnel into the top of the column and pour the sodium sulfate into the column to the correct height.

Support the column in an upright position by means of a clamp attached to a metal ring stand. Prewash the column with approximately 50 mL methylene chloride followed by approximately 50 mL of the elution solvent if different from methylene chloride.

9.1.3 Kuderna-Danish (K-D) apparatus:

9.1.3.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Use a ground-glass stopper to prevent evaporation of the extract.

9.1.3.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, claps or safe-T joint.

9.1.3.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

9.1.3.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

9.1.4 Nitrogen blowdown module: Module (Reacti-therm from Pierce Chemical Company, Rockford, Illinois or equivalent) equipped with Luer-Lock blunt tip needles and a source of N_2 gas passed through an activated carbon column (Supelpure HC 2-2445 or equivalent). The module should accommodate aluminum blocks or a water bath to hold the concentrator tubes.

9.1.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or Teflon or equivalent).

9.1.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath must be used in a hood.

9.1.7 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap. Amber vials are preferred.

9.1.8 pH indicator paper: pH range including the desired extraction pH.

9.1.9 Heating mantle: Rheostat controlled. Alternatively, a hot plate may be used as a heating unit.

9.1.10 Syringe: 5-mL, or other suitable equipment to deliver small volumes of solvent for rinsing such as Pasteur pipets.

9.1.11 Graduated cylinder: 1-liter, 500-mL and 100-mL glass cylinders.

9.1.12 Plastic tubing: New plastic tubing must have the internal walls rinsed several times with hexane before use with the Reacti-therm heating module.

9.1..13 Erlenmeyer flask: 250-mL

9.1.14 Glass equipment supports: Ring stand or similar support with a clamp attached to support either the extractor body or the drying column.

9.1.15 Separatory funnel: 2-liter glass funnel with stopcock and stopper of Teflon.

9.1.16 Glass equipment supports: Ring stand with large metal ring attached to support the glass separatory funnel and a clamp attached to support the drying column in an upright position.

9.1.17 Sonicator and associated equipment:

9.1.17.1 **Sonicator:** Ultrasonic Cell Disrupter - horn-type sonicator with a minimum power wattage of 375 and pulsing capability (Heat Systems - Ultrasonics, Inc., Model W-385 [475 Watts] or equivalent). See Table 2 for daily tuning instructions.

9.1.17.2 **Sonicator Titanium Tips:** Tapped disrupter horns - ½-inch (No. 200) and ¾-inch (No. 207) (Heat Systems - Ultrasonics, Inc. or equivalent).

9.1.17.3 Sonicator Titanium Tips: Standard tapered 1/8-inch microtip ultrasonic probe (Heat Systems - Ultrasonics, Inc. or equivalent).

9.1.17.4 **Sonabox:** Optional damper box to contain sonicator during operation. (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

9.1.17.5 **Sonicator horn support equipment:** Vinyl-coated clamp attached to heavy-duty ring stand. Secure the clamp on the chrome housing of the sonicator convertor only. The movement of the horn will be restricted if the clamp is placed on the driver or the horn sections. The convertor may also be hand-held during use.

9.1.18 Balance: Top-loading, capable of weighing to 0.01 g.

9.1.19 Glass scintillation vials: At least 10-mL with Teflon-lined screw-cap.

9.1.20 Spatula: Stainless steel or Teflon.

9.1.21 Beakers: 400-mL.

9.1.22 Filtration apparatus:

9.1.22.1 **Glass funnel:** 80-mm or of sufficient size to contain filter paper.

9.1.22.2 **Filter paper:** Whatman No. 41 or equivalent.

9.2 ANALYSIS

9.2.1 Packed GC Column: 100/200 mesh Supelcoport coated with 1.5% SP2250/1.95% SP2401.

9.2.2 Wide bore capillary column: DB-608 (ID >0.32 mm) 30 mL x 0.53 mm ID, 0.03 μm film thickness.

9.2.3 Fused-Silica Capillary GC Column: RTX-1701, 30 mL x 0.53 mm ID, 0.50 μm film thickness (Restek).

9.2.4 Gas Chromatographs, Data Systems, and Recorders.

9.2.5 Balance: Analytical, capable of weighing to 0.0001 g.

9.2.6 Syringes.

10.0 REAGENTS

10.1 EXTRACTION

10.1.1 Reagent water: Deionized water passed through an activated carbon column.

10.1.2 Sodium hydroxide solution, 10 N: Dissolve 40 g ACS grade NaOH in reagent water. Dilute to 100 mL with reagent water.

10.1.3 Sodium sulfate: ACS grade granular, anhydrous. Purify by heating at 400°C for at least 4 hr in a shallow tray.

10.1.4 Sulfuric acid (H_2SO_4) solution (1:1): Slowly and with caution, add 50 mL of reagent grade H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

10.1.5 Extraction/exchange solvents: Methylene chloride, hexane, cyclohexane, acetonitrile. (See LSG Procedure AP-001, Reagent Screening, for grades and pre-screening procedure.)

10.1.6 Nitrogen (N_2) gas: Zero grade gas dried by filtering through a column of activated carbon.

10.1.7 Stock standards: Materials prepared from pure standard materials or purchased as certified solutions. Base/neutral and acid stock standards are prepared in methylene chloride.

Store stock standard solutions in Teflon-lined screw cap, glass containers at 4°C. Replace these solutions after six months or sooner if comparison with quality control check samples indicate a problem.

The spiking solution concentrations listed in Table 4 are approximate. **However, the exact concentration of each spiking solution must be accurately known.**

10.1.8 Clean sand: Reagent grade sand (e.g., Ottawa sand or sea sand) muffled at 400°C for 4 hours (minimum).

10.2 ANALYSIS

10.2.1 Reagent water: Deionized water passed through an activated carbon column.

10.2.2 Solvents: Acetone, benzene, hexane and methanol of pesticide quality or equivalent.

10.2.3 Stock Standard Solutions: Prepare from pure standard material or purchase commercially. Prepare stock standard solutions in toluene.

Target Pesticide/PCB Stock Standard Solutions, 5000 µg/mL - Purchase commercially or prepare by dissolving 0.050 g of pure material in 10.0 mL hexane.

10.2.4 Surrogate, Internal and Matrix Spiking Standard Solutions: Prepare the indicated solutions as follows:

10.2.4.1 **Pesticide/PCB Surrogate Spiking Solutions** - Prepare a 50 µg/mL tetrachloro-m-xylene and decachlorophenyl stock solution in acetone. The concentration for each surrogate in all standard solutions is 0.05 µg/mL.

10.2.4.2 **Pesticide/PCB Matrix Spiking Solutions** - Prepare the following solutions in methanol at the indicated concentrations.

- Prepare a LLW matrix spiking solution in methanol containing the following compounds at the indicated concentrations. (1 mL is added to samples at the start of extraction. Extract final volume is 10 mL.)

0.2 µg/mL	Aldrin
0.2 µg/mL	Endrin
0.4 µg/mL	4,4'-DDT
0.1 µg/mL	a-BHC
0.2 µg/mL	b-BHC
0.2 µg/L	d-BHC
0.4 µg/L	4.4'-DDD
0.2 µg/L	4.4'-DDE
0.2 µg/L	Endosulfan I
0.25 µg/L	Methoxychlor
0.2 µg/L	Heptachlor Epoxide
0.4 µg/L	Endoosulfan Sulfate
5 µg/L	PCB-1242
5 µg/L	PCB-1260

- Prepare a LLS/MLS Matrix Spiking Solution in methanol containing the following compounds at the indicated concentrations. (50 µL is

added per 30 g of sample (LLS) or 50 µL is added per 1 g of sample (MLS) at the start of extraction. Extract final volume is 10 mL.)

4 µg/mL	Aldrin
4 µg/mL	Endrin
8 µg/mL	4,4'-DDT
2 µg/mL	a-BHC
4 µg/mL	b-BHC
4 µg/L	d-BHC
8 µg/L	4.4'-DDD
4 µg/L	4.4'-DDE
4 µg/L	Endosulfan I
4 µg/L	Methoxychlor
4 µg/L	Heptachlor Epoxide
8 µg/L	Endoosulfan Sulfate
5 µg/L	PCB-1242
5 µg/L	PCB-1260

10.2.5 Pesticide Breakdown Check: Prepare a solution containing the following compounds in hexane.

Compound	µg/mL
Endrin	0.01
DDT	0.02

10.2.6 Pesticide Primary/Confirmation Analysis Standards:

10.2.6.1 For the primary analysis and for the confirmation analysis use the standard concentrations listed on Table 6. These compounds may be combined into one mixed standard, Individual AB.

10.2.6.2 Alpha-Chlordane, gamma-Chlordane, and DBC are mixed into a separate standard. The concentrations for alpha-Chlordane and gamma-Chlordane are 0.02 mg/mL for each. The standard also contains 0.05 µg/mL decachlorophenyl and tetra-m-xylene.

10.2.7 PCB Primary/Confirmation Analysis Standard: The concentrations of the multi-response compounds are listed below for the primary and confirmation analyses.

Compound	Concentration (µg/mL)
Toxaphene	0.50

Aroclor - 1016	0.50
Aroclor - 1221	0.50
Aroclor - 1232	0.50
Aroclor - 1242	0.50
Aroclor - 1248	0.50
Aroclor - 1254	0.50
Aroclor - 1260	0.50

10.2.8 Toxaphene Standard Solutions: Prepare 0.5, 1.0 and 2.0 µg/mL toxaphene solutions, each containing 1.0 µg/mL decachlorophenyl and tetra-m-xylene, in hexane.

11.0 REFERENCES

11.1 U.S. EPA SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Volume IB, 1986; Methods 3500, 3510, 3520, 3550, and 8080.

11.2 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984, Method 608.

11.3 U.S. EPA Contract Laboratory Program, "Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration", OLM01.8

TABLE 1

PESTICIDE/PCB REPORTING LIMITS FOR TCL AND PRIORITY POLLUTANT ANALYSES

Compound	LLW (µg/L)	LLS[1] (µg/kg)
alpha-BHC	0.05	8
beta-BHC	0.05	8
delta-BHC	0.05	8
gamma-BHC (Lindane)	0.05	8
Heptachlor	0.05	8
Aldrin	0.05	8
Heptachlor Epoxide	0.05	8
Endosulfan I	0.05	8
Dieldrin	0.1	16
4,4'-DDE	0.1	16
Endrin	0.1	16
Endosulfan II	0.1	16
4,4'-DDD	0.1	16
Endosulfan Sulfate	0.1	16
4,4'-DDT	0.1	16
Endrin Ketone	0.1	16
Endrin Aldehyde	0.1	16
Methoxychlor	0.5	80
alpha-Chlordane	0.5	80
gamma-Chlordane	0.5	80
Toxaphene	1	160
Aroclor-1016	0.5	80
Aroclor-1221	0.5	80
Aroclor-1232	0.5	80
Aroclor-1242	0.5	80
Aroclor-1248	0.5	80
Aroclor-1254	1	160
Aroclor-1260	1	160

[1] MLS required reporting limits are 15 times those of LLS.

TABLE 2

PESTICIDE/PCB REPORTING LIMITS FOR RESIDENTIAL WELL ANALYSES

Compound	Target PQL (µg/L)	MDL Rtx35 (ug/L)	MDL Rtx1701 (ug/L)
alpha-BHC	0.01	0.004	0.003
beta-BHC	0.01	0.003	0.006
delta-BHC	0.01	0.002	0.002
gamma-BHC	0.01	0.002	0.003
Heptachlor	0.01	0.003	0.003
Aldrin	0.01	0.006	0.002
Heptachlor Epoxide	0.01	0.003	0.004
Endosulfan I	0.01	0.005	0.004
Dieldrin	0.02	0.006	0.006
4,4'-DDE	0.02	0.005	0.006
Endrin	0.02	0.004	0.006
Endosulfan II	0.02	0.009	0.004
4,4'-DDD	0.01	0.004	0.006
Endosulfan Sulfate	0.02	0.02	0.008
4,4'-DDT	0.02	0.005	0.009
Endrin Ketone	0.02	0.004	0.005
Methoxychlor	0.1	0.07	0.04
alpha-Chlordane	0.01	0.01	0.002
gamma-Chlordan	0.01	0.002	0.003
Toxaphene	1	0.3	0.5
Aroclor-1016	0.2	0.08	0.03
Aroclor-1232	0.4	0.006	0.02
Aroclor-1242	0.2	0.07	0.05
Aroclor-1248	0.2	0.2	0.02
Aroclor-1254	0.2	0.09	0.04
Aroclor-1260	0.2	0.07	0.03

TABLE 3

Spiking Solutions

Test	QC Solution	Solvent	Sample Matrix: Spike Added	Analyte(s)	Concentration of Spike Solution*
Pesticides/PCBs	Matrix Spike	Hexane	Water: 1.0 mL/1000 mL sample[1]	Lindane Heptachlor Aldrin Dieldrin Endrin 4,4'-DDT	0.2 µg/mL 0.2 µg/mL 0.2 µg/mL 0.5 µg/mL 0.5 µg/mL 0.5 µg/mL
Pesticides/PCBs	Matrix Spike	Methanol	LLS: 50 µL/30g sample[1] MLS: 50 µL/1g sample[1] Soxhlet: 50 µL/10 g sample[1]	Lindane Heptachlor Aldrin Dieldrin Endrin 4,4'-DDT	2 µg/mL 2 µg/mL 2 µg/mL 5 µg/mL 5 µg/mL 5 µg/mL
Pesticides/PCBs	Surrogate Spike	Acetone	Water: 1.0 mL/1000 mL sample	TCMX[2] DCB[2]	0.2 µg/mL 0.2 µg/mL
Pesticides/PCBs	Surrogate Spike	Acetone	LLS: 1.0 mL/30 g sample[1] Soxhlet: 1.0 mL/10 g sample[1]	TCMX[2] DCB[2]	0.2 µg/mL 0.2 µg/mL

TABLE 4

Tuning Procedures for Ultrasonic Cell Disrupter, Model W-385

Tune the sonicator daily as follows:

1. Place power switch (ON/OFF/TUNE) in the "OFF" position.
2. Turn the timer to the "HOLD" position.
3. Turn the output control knob fully counter-clockwise, below setting "1" for minimum amplitude.
4. Push and hold the power switch down in the "TUNE" position (it is spring loaded in this position and must be held during tuning).
5. Slowly turn the output control knob to setting "10" (maximum amplitude) taking care not to exceed 100%.
   - If the meter approaches 100%, lower the control knob setting to about "5" and continue with steps 6 through 9. Then raise the setting to "10" and retune.
   - If the generator has been thrown far off resonance, several increments between settings "5" and "10" may be required before the knob can be set to "10" without exceeding 100% on the meter.
6. Turn the tuning knob in whichever direction will cause the meter needle to move toward zero (0).
7. Continue turning the tuning knob in that same direction until the needle stops moving and then begins to move in a reverse direction.
8. Reverse the tuning knob very slowly to return the meter needle to its lowest reading (that "null" point at which any motion of the tuning knob in either direction will cause the needle to deflect away from zero).
9. Return the output control knob to minimum setting (fully counter-clockwise) and release the power switch. The generator is now tuned properly.

TABLE 5

GC OPERATING CONDITIONS

Parameters	DB608-FSC[2] Capillary Column	RTX-1701[2] Capillary Column
Oven Temperature[1]	185°C for 5 minutes, increase to 250°C at 5°C/minute	175°C for 5 minutes, increase to 260°C at 8°C/minute
Injection Temperature	230°C	200°C
Detector Temperature	320°C	310°C
Column Specifications	30 mL x 0.53 mm I.D.	30 mL x 0.25 mm I.D.
Flow Rate/Gas	7 mL/minute, Helium	0.3 mL/minute (approx.), Helium
Injection Volume	2 µL	2 µL

Parameters	Packed Column
Oven Temperature[1]	195°C, Isothermal
Injection Temperature	230°C
Detector Temperature	320°C
Column Specifications	1.5% SP-2250/ 1.95% SP-2401
Flow Rate/Gas	30 mL/minute, Helium
Injection Volume	4 µL

[1] Oven temperatures may vary from instrument to instrument. Temperature program used is documented in the run log for each run.

[2] Or equivalent column model.

TABLE 6

INITIAL CALIBRATION STANDARDS

Ind. A	Level 1 µg/mL	Level 2 µg/mL	Level 3 µg/mL	Level 4 µg/mL	Level 5 µg/mL
TCMX	0.05	0.05	0.05	0.05	0.05
G-BHC	0.005	0.01	0.02	0.04	0.045
Heptachlor	0.005	0.01	0.02	0.04	0.045
Aldrin	0.005	0.01	0.02	0.04	0.045
Hept. Epoxide	0.005	0.01	0.02	0.04	0.045
A-Endosulfan	0.005	0.01	0.02	0.04	0.045
Dieldrin	0.005	0.01	0.02	0.04	0.045
B-Endosulfan	0.005	0.01	0.02	0.04	0.045
DDT	0.01	0.02	0.04	0.08	0.085
End. Aldehyde	0.00625	0.0125	0.025	0.05	0.055
DCB	0.05	0.05	0.05	0.05	0.05
Methoxychlor	0.03	0.045	0.06	0.09	0.125
Ind. B					
TCMX	0.05	0.05	0.05	0.05	0.05
A-BHC	0.005	0.01	0.02	0.04	0.045
B-BHC	0.01	0.02	0.04	0.08	0.085
D-BHC	0.005	0.01	0.02	0.04	0.045
Aldrin	0.005	0.01	0.02	0.04	0.045
DDE	0.005	0.01	0.02	0.04	0.045
Endrin	0.005	0.01	0.02	0.04	0.045
DDD	0.005	0.01	0.02	0.04	0.045
Endosulfan sulfate	0.005	0.01	0.02	0.04	0.045
DCB	0.05	0.05	0.05	0.05	0.05

TCMX = Tetrachloro-m-xylene
DCB = Decachlorophenyl

TABLE 7

ORGANIC EXTRACTION LAB SAMPLE DESCRIPTION NOTES			
#	CHARACTERISTICS	#	CHARACTERISTICS
	Color As Received	20	Oil smell
1	Milky white	21	Sulfur smell
2	Yellow	22	Vinegar smell
3	Orange	23	Fish smell
4	Pink		**Concentration**
5	Brown	31	Very volatile, concentrated fast
6	Black	32	Very foamy, concentrated slow
7	Blue	33	Bumps, splatters, boils sluggishly
8	Green	34	Stopped concentrating before appropriate volume
9	Red	35	Particulate fallout
10	Purple	36	Phase separation
11	Grey	37	Nitrogen Blowdown req.
12	Turned with add of NaOH		**Emulsion**
13	Turned with add of H_2SO_4	41	Slight-needed centrifugation
14	Clear	42	Moderate-needed centrifugation
15	Opaque	43	Dense-centrifugation not good
	Odor As Received		**pH**
16	Strong	46	Basic
17	Very strong	47	Acidic
18	Phenol smell	48	Buffered
19	Solvent smell (paint)	49	Over 5 mL NaOH
	pH (Continued)	62	Wood
50	Over 100 mL NaOH	63	Very Fine Dust
51	Over 5 mL H_2SO_4	64	Clay
52	Over 10 mL H_2SO_4	65	Tar
	Soil Consistency	66	Filtered slow
56	Rocks	67	Viscous
57	Very Moist		**TCLP**
58	Sludge	71	Routine
59	Vegetation	72	CLP
60	Carbon	73	Filter
61	Ropes		

TABLE 8

QC Limits

QUALITY CONTROL TEST FILE
GC - PESTICIDES/PCBs (8080/608)
WATER, PM: E110 AND E113, AM: G30
DECEMBER 1993

Compound	Combo Number	Precision as RPD					Percent Recovery of Lab Contrl Standards						Percent Recovery of Matrix Spikes					
		WL	CL	X	S	Cpk[1]	WL	CL	X	S	Cpk[1]		95% CI	99% CI	X	S		
4,4'-DDD	....	....	≤20%[4]	....	....	....	....	20.7-153[11]	....	....	....		....	....	....	....		
4,4'-DDE	....	....	≤20%[4]	....	....	....	....	28.2-156[11]	....	....	....		....	....	....	....		
4,4'-DDT	GC50	....	≤48%	....	....		....	12.7-171[11]	....	....	....		47.4-161	19.5-189	104.19	28.22		
aldrin	GD11	....	≤56%	....	....		....	34.7-131[11]	....	....	....		62.4-143	42.2-163	102.55	20.09		
alpha-BHC	GD12	....	≤20%[4]	....	....	....	86.3-122	77.4-131	104.15	8.93	....		72.7-137	56.7-153	104.76	16.01		
alpha-chlordane	....	....	≤20%[4]	....	....	....	....	36.6-127[11]	....	....	....		....	....	....	....		
beta-BHC	....	....	≤20%[4]	....	....	....	....	28-135[11]	....	....	....		....	....	....	....		
delta-BHC	GD16	....	≤20%[4]	....	....	....	87.5-121	79.1-130	104.50	8.48	....		73.5-139	56.9-156	106.40	16.50		
dieldrin	GD19	....	≤46%	....	....		....	23.3-159[11]	....	....	....		66.4-141	47.8-159	103.56	18.60		
endosulfan I	....	....	≤20%[4]	....	....	....	....	33.5-164[11]	....	....	....		....	....	....	....		
endosulfan sulfate	....	....	≤20%[4]	....	....	....	....	13.4-157[11]	....	....	....		....	....	....	....		
endrin	GD23	....	≤52%	....	....		....	17.3-160[11]	....	....	....		66.5-151	45.3-172	108.85	21.18		
gamma-BHC (lindane)	GD26	....	≤64%	....	....		88.4-122	79.9-131	105.38	8.49	....		55.2-144	33.0-166	99.59	22.18		
gamma-chlordane	....	....	≤20%[4]	....	....	....	....	36.6-127[11]	....	....	....		....	....	....	....		
heptachlor	GD28	....	≤49%	....	....		....	24.9-117[11]	....	....	....		59.0-138	39.1-158	98.66	19.84		
heptachlor epoxide	....	....	≤20%[4]	....	....	....	....	35.5-152[11]	....	....	....		....	....	....	....		
methoxychlor	GD30	....	≤20%[4]	....	....	....	....	61.5-159[11]	....	....	....		77.8-143	61.5-159	110.47	16.33		
PCB-1242	GD41	....	≤20%[4]	....	....	....	....	25.8-163[11]	....	....	....		63.4-141	43.9-161	102.33	19.47		
PCB-1260	GD44	....	≤20%[4]	....	....	....	....	16.7-130[11]	....	....	....		73.6-131	59.3-145	102.02	14.31		
toxaphene	....	....	_20%[4]	....	....	....	....	32.1-135[11]	....	....	....		....	....	....	....		
decachlorobiphenyl(S)	GG48	NA	NA	NA	NA	NA	80.6-157	61.5-176	118.89	19.14	....		NA	NA	NA	NA		

Table 8
QC Limits (cont'd)
Page Two

QUALITY CONTROL TEST FILE
GC - PESTICIDES/PCBs (8080/608)
WATER, PM: E110 AND E113, AM: G30
DECEMBER 1993
PAGE 2

Compound	Combo	Precision as RPD					Percent Recovery of Lab Control Standards					Percent Recovery of Matrix Spikes			
		WL	CL	X	S	Cpk[1]	WL	CL	X	S	Cpk[2]	95% CI	99% CI	X	S
tetrachloro-m-xylene(S)	0047	NA	NA	NA	NA	NA	72.2-147	53.5-166	109.71	18.73	....	NA	NA	NA	NA
nonachlorbiphenyl(S)	GD45	NA	NA	NA	NA	NA	93.6-127	85.3-135	110.15	8.29	....	NA	NA	NA	NA

Table 8
QC Limits (cont'd)
Page Three

QUALITY CONTROL TEST FILE
GC - PESTICIDES/PCBs (8080/608)
SOIL, PM: E121SLLR AND E123SLLR, AM: G30
DECEMBER 1993

Compound	Combo	Precision as RPD					Percent Recovery of Lab Control Standards						Percent Recovery of Matrix Spikes					
		WL	CL	X	S	Cpk[1]	WL	CL	X	S	Cpk[1]	95% CI	99% CI	X	S
4,4'-DDD	....	....	≤40%[4]	....	....	....	....	20.7-153[11]	....	....	....	....	....	....	....
4,4'-DDE	....	....	≤40%[4]	....	....	....	....	28.2-156[11]	....	....	....	....	....	....	....
4,4'-DDT	....	....	≤40%[4]	....	....	....	....	12.7-171[11]	....	....	....	....	....	....	....
aldrin	....	....	≤40%[4]	....	....	....	....	34.7-131[11]	....	....	....	....	....	....	....
alpha-BHC	....	....	≤40%[4]	....	....	....	....	26.5-144[11]	....	....	....	....	....	....	....
alpha-chlordane	....	....	≤40%[4]	....	....	....	....	36.6-127[11]	....	....	....	....	....	....	....
beta-BHC	....	....	≤40%[4]	....	....	....	....	24-135[11]	....	....	....	....	....	....	....
delta-BHC	....	....	≤40%[4]	....	....	....	....	16.6-152[11]	....	....	....	....	....	....	....
dieldrin	....	....	≤40%[4]	....	....	....	....	23.3-159[11]	....	....	....	....	....	....	....
endosulfan I	....	....	≤40%[4]	....	....	....	....	33.5-164[11]	....	....	....	....	....	....	....
endosulfan sulfate	....	....	≤40%[4]	....	....	....	....	13.4-157[11]	....	....	....	....	....	....	....
endrin	....	....	≤40%[4]	....	....	....	....	17.3-160[11]	....	....	....	....	....	....	....
gamma-BHC [lindane]	....	....	≤40%[4]	....	....	....	....	21.0-138[11]	....	....	....	....	....	....	....
gamma-chlordane	....	....	≤40%[4]	....	....	....	....	36.6-127[11]	....	....	....	....	....	....	....
heptachlor	....	....	≤40%[4]	....	....	....	....	24.9-117[11]	....	....	....	....	....	....	....
heptachlor epoxide	....	....	≤40%[4]	....	....	....	....	35.5-152[11]	....	....	....	....	....	....	....
methoxychlor	....	....	≤40%[4]	....	....	....	....	61.5-159[12]	....	....	....	....	....	....	....
PCB-1242	GE28	....	≤27%	....	....	....	....	25.8-163[11]	....	....	....	58.0-141	37.2-162	99.65	20.83
PCB-1260	GE31	....	≤33%	....	....	....	....	16.7-130[11]	....	....	....	63.6-125	48.3-140	94.34	15.36
toxaphene	....	....	≤40%[4]	....	....	....	....	32.1-135[11]	....	....	....	....	....	....	....
decachlorbiphenyl(S)	GG50	NA	NA	NA	NA	NA	69.5-152	48.6-173	110.78	20.63	....	NA	NA	NA	NA

Table 8
QC Limits (cont'd)
Page Four

QUALITY CONTROL TEST FILE
GC - PESTICIDES/PCBs (8080/608)
SOIL, PM: E121SLLR AND E123SLLR, AM: G30
DECEMBER 1993
PAGE 2

Compound	Combo	Precision as RPD					Percent Recovery of Lab Control Standards					Percent Recovery of Matrix Spikes			
		WL	CL	X	S	Cpk[1]	WL	CL	X	S	Cpk[2]	95% CI	99% CI	X	S
tetrachloro-m-xylene(S)	GO49	NA	NA	NA	NA	NA	30.0-144	1.4-173	87.28	28.63	----	NA	NA	NA	NA
nonachlorbiphenyl(S)	GE32	NA	NA	NA	NA	NA	81.6-125	70.8-136	103.3	10.86	----	NA	NA	NA	NA

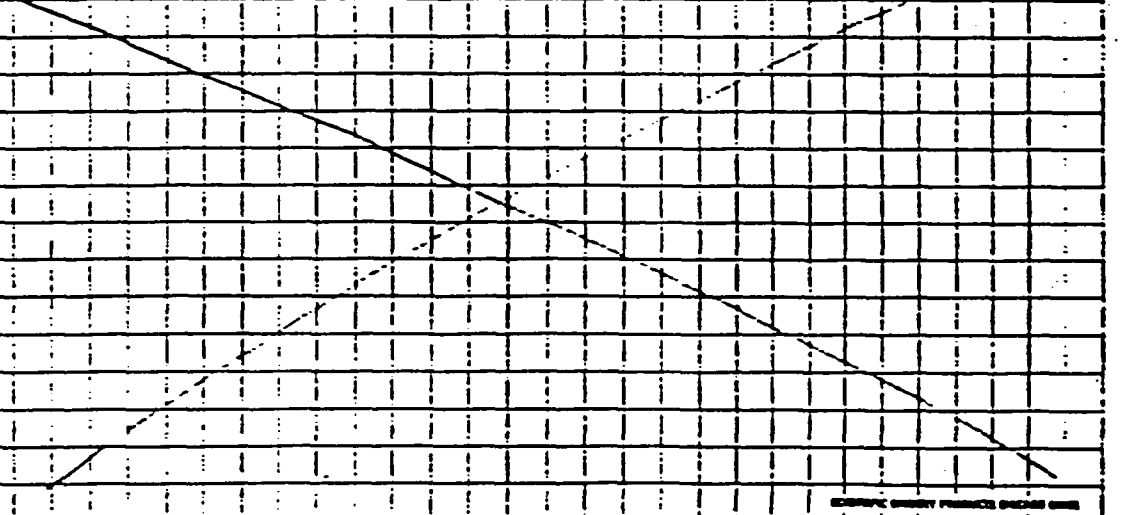
FIGURE 1

Extraction Log

TITLE EASTLL LLS BNA EXAMPLE ONLY **PROJECT NO.** **BOOK NO.** 150-91 **52**

SAMPLE #	ALIQUOT	Na_2SO_4	FINAL VOL.	DESCRIPTION	DUPLICATE
PI70943	30.02g	29.97g	1.0 mL	64	
PI70945	30.60g	29.99g		64	
PI70946	30.05g	30.05g		64	
PI70947	29.97g	30.02g		64	
PI70948	30.02g	29.97g		64	
PI70949	30.01g	30.04g		64	
PI70949 MS	29.97g	29.99g			
PI70949 MSD	29.99g	30.01g			
PI70950	30.01g	29.92g		64, 56, 57	
PI70951	30.03g	29.96g			
PI70955	29.99g	30.02g			
PI70959	29.99g	30.04g		36.57	
BLANK					

1.0 mL BNA surrogate (1-37-91-107) added to all samples.
1.0 mL BNA spike (2-37-91-125) added to all 949 MS/MSD.
Batch No.: 1247
Extraction: 8/5/91 8:15am - 10:15 am Frank Analyst
Concentration: 8/5/91 2:10pm - 3:30 pm Frank A / Second Analyst
Final Concentration Method: Water Bath



SIGNATURE DATE

DISCLOSED TO AND UNDERSTOOD BY DATE WITNESS Frank Smith DATE 8/6/91

FIGURE 2

GC Injection Log

TITLE GC - Pesticides / PCBs (PACB-GC) EXAMPLE ONLY
PROJECT NO.
BOOK NO. P313-27
107

Date 7-21-92 | Packing DB608
Sample Water | Length 30m
Injection Autoauto | Diameter 0.53mm
Chart Speed — | Oven Temp. 185-5-5-200-15
N2 Flow 30ml/min | Inj. Temp. 235C
Detector ECD#4 | Det. Temp. 325C

Run #	Sample	Dilution	Amount Ext - Final Vol (mL)	Client / Comments
1	Hexane	↓	↓	Solvent Blank
2	Eval A			↓
3	Eval B			
4	Eval C			
5	Int A			
6A	Int B			
6	Toxaphene			
7	Chlordane			
8	AR 1660			
9	AR 1221			
10	AR 1232			
11	AR 1242			
12	AR 1248			
13	AR 1254	↓	↓	↓
14	P205042 5x	200 µL/1mL	1L - 10mL	HNUS
15	P205047 5x	↓	↓	↓
16	P204902 #1	↓		
17	P204902 #2			
18	P204902 Tk		↓	↓
19	Eval B	↓	—	—
20	P205522 10x	100 µL/1mL	1L - 10mL	HNUS
21	P205727 10x	↓	↓	↓
22	P206183	—	↓	BLK

Work contd on page 108.

SCIENTIFIC BINDERY PRODUCTS CHICAGO

SIGNATURE Cane Analyst
DATE 7/21/92

DISCLOSED TO AND UNDERSTOOD BY Frank Smith
DATE 7-23-92
WITNESS
DATE

FIGURE 3

GC Assignment Sheet

GC Assignment Sheet (10-Jul-92 Samples 205522 - 205522)

Due Date: ___-___-___

Date entered and init.: 07-24-92 SAM
Approved and init.: 7-28-92 RSC

Sample: P205522 Test: G120V Type: ORIG
Analysis Number: 1 Anls. Ref. Number:
Analyst (Emp#) Number: 0940
Date Analyzed: 7 20 92 Time: 17:17
Instrument: GC 6
Book: 44 92 Page: 33
Sample Description: ICLP LLCS BLANK BATCH 0014
Client: HALLIBURTON NUS ENVIRONMENTAL CORP
UNITS: ug/L BLANK SAMPLE #: P205522 RUN BATCH #: 11266 11332
PM: E110VE AM: G30VE- CASE ID: not available SDG: not available

Run File	Dilution	Log Page	Anlst/Processor(Emp#)
	100X		

Time Sampled: Received 08-JUL-92
Original (vol/wt): 100ml
Final (vol): 1ml

ORGANOCHLORINE PESTICIDES AND PCB's

ANALYTE	REPORTING LIMIT	RESULT	QUALIFIER
4,4' DDD	0.1		
4,4' DDE	"		
4,4' DDT	"		
Aldrin	0.05		
Chlordane	"	13.0	
Dieldrin	0.1		
Endosulfan I	0.05		
Endosulfan II	0.1		
Endosulfan sulfate	"		
Endrin	"	14.9	
Endrin aldehyde	"	"	
Heptachlor	0.05	133	
Heptachlor epoxide	"		
PCB-1016	0.5		
PCB-1221	"		
PCB-1232	"		
PCB-1242	"		
PCB-1248	"		
PCB-1254	"		
PCB-1260	"		
Toxaphene	"		
alpha-BHC	0.05		
beta-BHC	"		
delta-BHC	"		
gamma-BHC (Lindane)	"	29.4	

EXAMPLE ONLY

SURROGATES		
Dibutylchlorendate	67113	Do

COMMENTS: _____

Special Instructions

Halliburton NUS
CORPORATION

NUS LABORATORY
5350 Campbells Run Road
Pittsburgh, Pennsylvania 15205

TEL: (412) 747-2500
FAX: (412) 747-2559

LABORATORY METHOD

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD

METHOD ID: CRA/SN-ICP
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD

1.0 SCOPE AND APPLICATION

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, hereafter referred to as ICP) is used to determine elements, primarily metals, in solution. Groundwaters, surface waters, effluents, leachates, soil/sediment, or waste can be analyzed using ICP following suitable digestion to solubilize the analytes.

This procedure is used for the simultaneous multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique.

Table 1 lists analytes and their corresponding wavelengths, reporting limits, and linear ranges. Instrument detection limits, as obtained from periodic detection limit studies, are updated and published quarterly.

This procedure is specific to the ARL Model 3560 simultaneous computer-controlled inductively coupled plasma - atomic emission spectrometer with background correction.

2.0 SUMMARY OF METHOD

A mixture of sample is acid digested on a hot plate and evaporated to a low volume. The digestate is cooled, filtered if necessary, and brought to final volume with reagent water.

Samples digestates are nebulized and the aerosol is transported to the plasma torch for excitation. Characteristic atomic line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and emission intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are collected and processed by a computer system.

A background correction technique compensates for variable background contributions to the determination of trace elements. Background is measured adjacent to analyte lines during sample analysis. The position selected for the

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Approvals:

Technical Operations Manager	Date 4/12/94	Group Leader	Date 4/12/94	Quality Assurance Director	Date 4/12/94

background intensity measurement, on either or both sides of the analytical line, is determined by the complexity of the spectrum adjacent to the analyte line. The chosen position must be as free of spectral interference as possible and must reflect the same change in background intensity as occurs at the analyte wavelength measured.

3.0 PROCEDURE

3.1 SAMPLE PRESERVATION

3.1.1 Store all water samples in either plastic or glass bottles preserved with nitric acid (to pH <2). Samples must be analyzed within six months.

3.1.2 Store all soil samples unpreserved in either plastic or glass containers. Samples must be analyzed within six months.

3.2 SAMPLE PREPARATION

3.2.1 Hot Plate Acid Digestion of Water Samples for Total Recoverable Metals Determination

a. Turn on the fume hoods and ensure that there is adequate air ventilation. Turn on hot plates to allow them to achieve initial digestion/evaporation temperature while samples are being prepared for digestion. Set Thermolyne hot plates at approximately 5 and Lindberg hot plates to 5.5 - 6.0.

b. Shake the sample bottle vigorously to achieve homogeneity. Immediately transfer 100 mL of the sample to a 150-mL Griffin beaker using a graduated cylinder.

c. Add 2 mL of concentrated nitric acid (HNO_3) and 5 mL of concentrated hydrochloric acid (HCl) then cover with a ribbed watch glass or similar device.

d. Place beaker on the hot plate in the hood and cautiously evaporate the sample to a volume of approximately 15-20 mL.

During evaporation, ensure that the sample DOES NOT BOIL and that no portion of the bottom of the beaker goes dry. If the sample goes to dryness, discard the sample and reprepare.

e. Cool the beaker. Rinse the watch glass with reagent water, collecting the washings in the beaker. Rinse the walls of the beaker with reagent water.

f. If visible solids are observed in any one of the samples in a batch, filter all digestates within that batch, including the associated quality control samples as outlined below. Otherwise, proceed to 3.2.1.g.

f.1 Assemble a filter funnel and Whatman #41 filter paper. Prerinse the filter/funnel apparatus with 1% HNO_3 solution.

f.2 Place a 100-mL volumetric flask under the funnel. Quantitatively transfer the contents of the beaker into the prerinsed filter/funnel apparatus with reagent water.

f.3 Rinse the filter paper thoroughly with reagent water. Rinse the tip of the funnel, collecting the washings into the volumetric flask. Proceed to 3.2.1.h.

g. If none of the digestates require filtration, quantitatively transfer the digestate to a 100-mL volumetric flask.

h. Bring the digestate to volume with reagent water and mix thoroughly by inversion.

i. Transfer the digestate to a prelabeled polyethylene bottle with a polyethylene-lined cap.

Obtain labels for sample bottles by using LIMS program ALABEL. This program prints labels, by sample batch, which lists the unique NUS Laboratory sample number, client, batch number, sample type (LCS, dup, orig), preparation description, date of preparation and initial/final volumes.

j. If a digestate analyzed by ICP is found to contain more than 6 mg/L silver, redigest the sample using a smaller sample aliquot in order to keep the analyte in solution.

3.2.2 Hot Plate Acid Digestion of Solid Samples for Total Metals Determination

a. Turn on the fume hoods and ensure that there is adequate air ventilation. Turn on hot plates to allow them to achieve initial digestion/evaporation temperature while samples are being prepared for digestion. Set Thermolyne hot plates at approximately 5 and Lindberg hot plates to 5.5 - 6.0.

b. Mix the sample to achieve homogeneity. Weigh a 1.00 ±0.01 g (wet weight) aliquot of sample into a 150-mL Griffin beaker. Record the weight to the nearest 0.01 g.

Note: If preforming boron and/or silicon determinations, either alone or along with other analytes, prepare the B/Si samples in fluted

Teflon beakers with Teflon lids. Place a fiberglass mat on the hot plate to prevent the Teflon beakers from melting or warping.

c. Add 10 mL of 1:1 nitric acid (HNO_3). Mix the sample to a slurry consistency and cover with a plain watch glass.

d. Place the beaker on the hot plate in the hood and cautiously reflux the sample for 15 minutes without boiling.

e. Allow the digestate to cool. Rinse the watchglass with a minimum of reagent water, collecting the rinsate in the beaker. Then add 5 mL of concentrated HNO_3. Place the beaker on the hot plate and reflux for 30 min.

f. Repeat step 3.2.2.e to complete the oxidation process.

g. Using a ribbed watch glass, place beaker on the hot plate in the hood and cautiously evaporate the sample to a volume of approximately 5 mL.

During evaporation, ensure that the sample does not boil and that no portion of the bottom of the beaker goes dry. If the sample goes to dryness, discard the sample and reprepare.

h. Cool the beaker and add 2 mL of reagent water and 2.5 mL of 30% hydrogen peroxide. Cover the beaker with the plain watch glass and gently warm the beaker to start the peroxide reaction. Heat until effervescence ceases, then cool the beaker.

CAUTION: Hydrogen peroxide may react vigorously. Care must be taken to avoid sample losses due to splattering during peroxide reaction.

i. Add 30% hydrogen peroxide in additional 2.5-mL aliquots with gentle warming until effervescence is minimal or until no change is observed in the sample's appearance. Do not add more than a total of 10 mL of 30% hydrogen peroxide to any one sample.

j. Add 5 mL of concentrated HCl and 10 mL of reagent water. Place covered beaker on the hot plate and reflux for 15 minutes. DO NOT BOIL.

k. Cool the beaker. Rinse the watch glass with a minimum of reagent water, collecting the washings in the beaker. Rinse the sides of the beaker with reagent water.

l. Filter all digestates, including the associated quality control samples, as outlined above in Section 3.2.1.f.

m. Transfer the digestate to a prelabeled polyethylene bottle with a polyethylene-lined cap.

Obtain labels for sample bottles by using LIMS program ALABEL. This program prints labels, by sample batch, which lists the unique NUS Laboratory sample number, client, batch number, sample type (LCS, dup, orig), preparation description, date of preparation and initial/final volumes.

n. If a digestate analyzed by ICP is found to contain more than 600 mg/kg silver (6.0 mg/L in the digestate), redigest the sample using a smaller sample aliquot in order to keep the analyte in solution.

3.3 PRELIMINARY OPERATION OF THE ICP

Note: The ARL Model 3560 main instrument is always left on to maintain consistent vacuum and temperature. See manufacturers' operator manual for information on starting-up the main instrument.

3.3.1 Press the **STAND** button located on the main instrument to turn on the torch stand unit. Turn on the computer and printer.

3.3.2 Hook up sample introduction pump:

a. Examine the sample tubing for flat spots or other wear from the pump. Replace the tubing as necessary.

b. Thread the sample tube around the pump then fasten the clamp to put tension on the tube.

c. Flip on the power toggle switch located on the pump unit.

d. Place the tip of the introduction tube into rinse water and let the rinse water flow through the sample tube.

3.3.3 Verify interlocks by checking that all four vertically-arranged lights on the torch stand unit are illuminated, then press **START** on the torch stand unit to light the plasma torch.

3.3.4 Prepare standards (see Section 9.0). Document standards preparation in the appropriate log book.

3.3.5 Document instrument status:

a. Press <ALT>/<F5> to open the ROUTINE option window then press <F1> to select "System Log/Alarm Status."

b. Enter <Y> for yes to save values to the status log database files. Press <F1> to print status report (see Figure 1 for example of status printout). The time of status measurement is considered the start of the run. Verify the correct date and time from the instrument status record. Otherwise return the computer system to the DOS prompt and correct the date and time before starting analyses for the day.

c. Document watts, volts, and currents onto the status printout: press each of the following buttons from the RF Generator Controls and record the display values.

- incident watts
- reflected watts
- plate volts x10
- plate current
- grid current mA
- drive volts x10

d. Measure and document flow rate onto the status printout: fill a 10-mL graduate with 10 mL of reagent water, time the pump for one minute beginning upon insertion of sample introduction tube into the graduate, measure flow as mL/min by recording the volume (mL) remaining in the graduate after one minute has elapsed.

3.3.6 Verify optical alignment:

a. Press <F5> to select "Check Optical Alignment" from the ROUTINE option window, then press <F2> to select "Digital Profile" from the program scheduler window.

b. Insert sample introduction tube into the profile standard (see Section 9.0); press <F2> to "Run Profile," then press <F1> to Profile.

c. Press <F8> after profile is complete to return to the program scheduler window, then press <F3> to select "Set/Plot Profile."

d. Plot five profile curves for the elements Mn, Cr, As, Sb, and Se by using the following key sequence: <F1>, graph #, element symbol.

Note: More than one curve may be plotted per graph (See Figure 2).
Example: Plot profile curve for Mn.

<F1> [plot]
[computer prompts: enter graph # 1-3]
Enter the number "1"
[computer prompts: select element]
Enter "Mn"
[computer automatically plots profile]

e. Set the new profile position by using the following key sequence: <**F5**>, <**F4**>, <**A**> for average, <**A**> for all elements, <**Y**> for yes, and <**F8**> to exit after setting position.

Example: Set the new profile position.

<**F5**> [plot profile]
<**F4**> [plot profile]
<**A**> [average]
<**A**> [all elements -- accepts average profile of all elements profiled]
<**Y**> [yes to confirm update of profile]
<**F8**> [exits from plot profile window]

f. Press <**Print Screen**> to print out a hard copy of the profile plotting. Press <**F8**> to exit.

3.4 CALIBRATION

3.4.1 Press <**ALT**>/<**F1**> for "set up," <**F4**> for "calibrate lines," and <**F2**> for "sequence standards."

3.4.2 Use arrow key to select "Pick Sequence File" then press <**ENTER**>. Check that all elements of interest are listed with the correct concentrations. Make changes as necessary, then press <**F8**> to save file.

3.4.3 Press <**F3**> to "run standards," use arrow key to select "manual calibration," pick file being used, then press <**F1**> to "run standards."

3.4.4 Aliquot 10.0 mL of each standard into individual sample cups then add 100 µL of 1000 mg/L yttrium internal standard to each standard and also to the blank (see Table 2 for analytical sequence).

Note: Yttrium internal standardization is not presently available on the ARL ICP 3560 Unit 2. Consequently, Unit 2 may be operated without Y additions to standards and samples, although a 1:5 serial dilution is required for routine samples.

3.4.5 Place the sample introduction tube into the first sample cup and hit any keyboard key to analyze that standard. Continue in this manner for all of the standards. When finished, press <**F8**> to save the data.

3.4.6 Press <**F5**> to "auto-refit curves." (Verify that the correlation coefficient is $\geq$ 0.995; Auto-Refit will print calibration data and save data.) When all analytes are regressed, the program scheduler appears (see Figure 3 for an example of this printout).

Note: The calibration curve may instead be manually fit by pressing <**F4**>. This may prove faster for runs with few elements (see the software users manual for details on this).

3.5 SAMPLE ANALYSIS

3.5.1 Press <**Alt**>/<**F2**> for "analyze," <**F1**> for "manual," then <**F2**> for "run unknowns."

3.5.2 Select "Continue," press <**ENTER**>, then press <**F4**> for "Name a File." Name the file using the following code:

AYYMMDDx

where A corresponds to ICP unit 1 (use B for unit 2), YY to the year, MM to the month, DD to the day, and x to an individually assigned employee ICP code.

Refer to Table 2 for sequence and to the QC section for criteria.

3.5.3 Press <**F1**> to "Analyze." Aliquot 10 mL of all standards and samples into disposable sample cups. Into each cup, spike 100 μL of 1000 ppm Y.

3.5.4 Place the introduction tube into a sample digestate then press <**Enter**>.

3.5.5 After the analysis is complete, the computer will return with the prompt "Enter Sample Identity 1." Type in the sample identity, then press <**ENTER**>.

3.5.6 Press <**F8**> to continue printing of the analysis.

3.5.7 Evaluate the results on the sample. Verify that each analyte is within its respective range and determine if the %RPD is within range (<20% for any result greater than 2x the reporting limit).

Note: If a silver result on an undiluted digestate exceeds 6.0 mg/L, do not accept the data. Initiate re-digestion using a smaller sample aliquot.

3.5.8 Highlight usable sample results on the instrument printout. Document the sample analysis and any discrepancies in the instrument log book.

3.5.9 Press <**ESC**> to return to the analyze mode for the next sample. Reanalyze the sample, if necessary, for any discrepancies (i.e., high %RPD must be rerun, overrange results must be run at a dilution).

3.5.10 Repeat steps 3.5.4 through 3.5.9 until all samples, calibration standards, blanks, etc. are analyzed.

3.6 CALCULATIONS

3.6.1 Read the metal result in mg/L directly from the instrument printout.

3.6.2 For aqueous samples report metal concentrations in mg/L using the following equation:

$$Metal_{(mg/L)} = A \times DF$$

where A = metal result in mg/L of sample digestate from calibration curve
DF = dilution factor, if necessary (final volume/initial volume)

Note: A dilution may have been used in sample preparation which must be taken in account in calculating the final results. See the sample logbook for unusual sample volumes.

3.6.3 For solid samples report metal concentrations as mg/kg, wet or dry weight, using the appropriate equation(s) below:

a. Solid samples - wet weight:

$$Metal_{(mg/kg\ wet)} = \frac{A \times V}{W}$$

where A = metal result in mg/L of sample digestate from calibration curve
V = final volume of processed sample in mL
W = wet weight of sample in grams

b. Solid samples - dry weight:

$$Metal_{(mg/kg\ dry)} = Metal_{(mg/kg\ wet)} \times \frac{100}{\%\ solids}$$

3.7 INSTRUMENT SHUT-DOWN

3.7.1 Press <**F8**> to continue, <**F8**> to exit, then <**Alt**>/<**F5**> to return to ROUTINE option window. Turn off the computer monitor.

3.7.2 Remove sample introduction tube from rinse water to drain tube.

3.7.3 Press **STOP** on the torch stand to extinguish the torch. Listen for the Argon to completely drain.

3.7.4 Turn off pump, then unfasten tube clamp to release the tension on the tubing.

3.7.5 Press **STAND** on the main instrument to turn off torch stand.

4.0 DATA COLLECTION

4.1 Document the following information in a bound lab notebook for each set of acid digestions performed. Entries must be made at the time of digestion. An example logbook entry is shown in Figure 4 and briefly described below:

- preparation method (PM) code.
- date/time performed and analyst(s) signature(s)/employee number(s).
- NUS Laboratory sample number and aliquot. Identify any quality control samples (method blank, LCS, dup/MS).
- spiking standards, by standard identification number and volumes used.
- batch number.

4.2 Document each ICP run in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. Following data reduction, complete the worksheet. Example logbook and worksheet entries are shown on Figures 5 and 6, respectively, and briefly described below:

- brief description of analysis (e.g., ICP Analysis).
- date and time analysis started and analyst(s) signature(s).
- NUS Laboratory sample number and sample aliquot. Identify any lab quality control samples (method blanks, MS/MSDs, LCSs).
- any dilutions used.
- spikes added, to include the spiking solution identification number and the volume of spike added for post-digestion spikes.
- comments regarding nonconforming conditions that were resolved within the analysis run.
- nonconformances where necessary.

4.3 Forward the following to data management from each analytical run:

- preparation raw data, including standards/spiking solutions preparation pages.

- analytical raw data, including logbook page(s), worksheet/assignment sheets, and instrument printouts.
- description of problems encountered and actions taken during sample preparation and analysis on corrective action records.
- initial and continuing calibration files from the instrument software system.
- sample and associated quality control sample files (method blanks, MS/MSDs, LCSs) from the instrument software system.
- any instrument maintenance documented in the instrument maintenance log.

5.0 QUALITY CONTROL

5.1 INSTRUMENT CONTROL CHECKS

5.1.1 High Standard

Before beginning the sample run, reanalyze the highest mixed calibration standard for each analyte as if it were a sample. Recovery must be 95.0-105%. If recovery exceeds the control limit, reanalyze the high standard. If the problem persists, terminate analysis, correct the problem, recalibrate and reverify the calibration.

5.1.2 Initial Calibration Verification (ICV)

Immediately after instrument calibration, verify and document the accuracy of the initial calibration for every analyte by running an Initial Calibration Verification (ICV) standard at each wavelength used for analysis. This standard is from a source independent of the calibration standards.

When measurements exceed the control limits of 90-110%, terminate analysis, correct the problem, recalibrate the instrument, and reverify the calibration before proceeding with the analysis sequence.

5.1.3 Initial Calibration Blank (ICB)

Analyze a calibration blank at each wavelength used for analysis immediately after the ICV.

If the absolute value of the blank result exceeds the reporting limit, terminate analysis, correct the problem, and recalibrate and verify the calibration. Reanalyze all samples and quality control checks analyzed since the last acceptable calibration blank.

5.1.4 Reporting Limit Standard

To verify linearity near the reporting limit for ICP analysis, analyze an ICP standard for all metals at two times the reporting limit from Table 1 at the beginning of each sample analysis run. The response for this standard must be discernible from the ICB as evident by a recovery of $\geq$ 50%. If recovery is less than 50%, reanalyze a fresh aliquot of the standard or terminate the analysis to correct the problem.

For standards 2x the IDL, a $\geq$50% recovery is not required: only a result discernable from the ICB.

5.1.5 ICP Interference Check Sample (ICS) Analysis

Refer to Table 3. To verify interelement and background correction factors, analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run, and every 8 hours of operation, whichever is more frequent.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferants and Solution AB consists of the analytes mixed with the interferants. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A, for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm$20% of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze all samples run since the last good ICS.

5.1.6 Continuing Calibration Standard (CCS)

To ensure calibration accuracy during each run, analyze a mid-range standard for continuing calibration verification. Analyze at a frequency of 10% and report the CCS for every wavelength used for the analysis of each analyte.

If the deviation of the continuing calibration standard is greater than the control limits of 90-110%, terminate analysis, correct the problem, recalibrate the instrument and reverify the calibration. Reanalyze all samples and quality control checks run since the last good calibration verification for the affected analytes.

5.1.7 Continuing Calibration Blank (CCB)

Analyze a calibration blank at each wavelength used for analysis after each continuing calibration verification standard.

If the absolute value of the blank result exceeds the reporting limit, terminate analysis, correct the problem, and recalibrate and verify the calibration. Reanalyze all samples and quality control checks analyzed since the last acceptable calibration blank.

5.2 SAMPLE PREPARATION CHECKS

5.2.1 Preparation Blank (PB) Analysis

A preparation blank, consisting of reagent water processed through sample preparation, is prepared and analyzed with each batch of up to 20 samples digested at the same time.

Evaluate the preparation blank results as follows:

a. If the absolute value of the concentration of the blank is less than or equal to the routine reporting limit, no correction of sample results is performed. Ideally, when sample results are observed down to the reporting limit, the preparation blank should not yield results greater than 50% of the reporting limit. However, this is impractical when the reporting limit is less than twice the instrument detection limit.

b. If any analyte concentration in the blank is above the routine reporting limit, the lowest acceptable concentration of that analyte in the associated samples must be 10x the blank concentration for sample results to be reported.

   Otherwise, all samples associated with the blank, with analyte concentration less than 10x the blank concentration and above the routine reporting limit, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.

c. If the concentration of the blank is below the negative routine reporting limit, then reanalyze (or redigest and reanalyze, depending upon the cause of the problem) all sample results below 10x the absolute value of the blank.

   Note: First, troubleshoot the calibration curve for the element in question. If the calibration yields an artificially high intercept, then recalibrate the element before reanalysis. Only consider redigestion as a last resort because this problem points to causes other than sample preparation.

5.2.2 Laboratory Control Sample (LCS) Analysis

A laboratory control sample (LCS) is prepared and analyzed for all target analytes for each matrix (water or solid/waste) with each batch of up to 20 samples digested together.

The aqueous LCS solution must be independent (i.e., from a different lot) from the calibration standards. Prepare and analyze one aqueous LCS for every batch of 20 samples digested at the same time.

Prepare and analyze one solid LCS, using each of the procedures applied to solid samples, for every batch of 20 samples digested at the same time. If an analyte of interest is not present in a reference material, spike that analyte into the LCS.

If the percent recovery for an LCS falls outside the control limits, redigest and reanalyze the samples associated with that LCS for the analyte(s) in question. Table 4 lists the current LCS limits. These statistically-based limits are updated semi-annually and subject to change.

When a new LCS (aqueous or solid) is procured, verify the standard prior to use with a real batch of samples. Verify by comparing the average recovery result of 4 undigested aliquots of the LCS with the true value (for waters) or comparing the average recovery of 4 digested samples on two consecutive days (for soils).

5.2.3 Spike Sample Analysis

The spike sample analysis provides information about the effect of the sample matrix on the digestion and measurement procedures. Add the spike before digestion prior to the addition of other reagents. Perform at least one spike sample analysis for every batch of 10 samples digested at the same time.

Refer to Table 5 for the analyte spiking levels.

If the spike recovery is not within the limits of 75-125%, qualify the data for that sample as follows:

> This sample was analyzed as a matrix spike. Recovery of the spike was outside the established acceptance limits. However, the preparation blank and laboratory control sample were found to be in control, indicating the presence of a matrix interference.

Calculate individual component percent recoveries (%R) as follows:

$$\%\ Recovery = \frac{(SSR - SR)}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Note: When the sample concentration is less than the reporting limit, use SR = 0 for purposes of calculating % Recovery.

When the sample concentration exceeds the spike concentration by a factor of four or more, the data is flagged and noted as follows:

Sample concentration greater than four times spike concentration.

5.2.4 Duplicate Sample Analysis

The duplicate sample provides information about the reproducibility of ICP results.

Prepare and analyze one duplicate sample for every 10 samples in a batch digested at the same time.

a. For results that

- are less than five times the reporting limit or
- one result is above five times the reporting limit and one is below

use a control limit of ±2x IDL or 20% for waters (±4 x IDL or 40% for soils).

b. For results that are greater than five times the reporting limit calculate the relative percent difference (RPD) as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

where RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

Limits for precision are listed in Table 4. However, precision limits default to 20% for waters (40% for soils) when the relative error in the reportable sample results exceeds the specified precision limits. The statistically-based limits are updated semi-annually and subject to change.

When precision is unacceptable, reanalyze the duplicate sample. If it remains nonconforming, redigest and reanalyze 25% of the positive results. If reanalysis results do not yield acceptable precision, redigest and reanalyze all samples and report the reanalysis results.

5.3 INSTRUMENT DETECTION LIMIT (IDL) DETERMINATION

Determine instrument detection limits for each instrument used, at least quarterly (every 3 calendar months) for CLP TAL analytes and biennially for non-TAL analytes. The IDLs must meet the reporting limits.

Determine the Instrument Detection Limits in µg/L as follows:

- Prepare a standard solution of each analyte in reagent water at a concentration 3-5x the manufacturer's suggested IDL initially, then 3-5x the previously determined IDL thereafter.

- Perform seven consecutive measurements of the standard on three nonconsecutive days.

  Perform each measurement as if it were a separate analytical sample followed by a rinse and/or any other procedure normally performed between analyses of separate samples.

  Calculate the mean and standard deviation for each set of seven measurements. The observed daily mean must fall within a factor of two of the true value for the data to be useful for the IDL study.

- Average the standard deviation values.

- Calculate the IDL (µg/L) by multiplying the average SD by 3.

  Determine and report IDLs for each wavelength used in the analysis of the samples.

5.4 METHOD DETECTION LIMIT STUDIES

A method detection limit (MDL) study for water analysis is performed annually according to 40 CFR 136, Appendix B. Statistically-based MDLs must be ≤ reporting limits for the method.

5.5 INTERELEMENT CORRECTIONS FOR ICP

Determine ICP interelement correction factors for TAL and non-TAL analytes annually, at a minimum. Determine correction factors for spectral interference due to Al, Ca, Cr, Fe, Mg, Mn, Ni, and V for all ICP instruments at all wavelengths used for each reported analyte. Report correction factors for

spectral interference due to analytes other than Al, Ca, Cr, Fe, Mg, Mn, Ni, and V if they were applied.

5.6 LINEAR RANGE ANALYSIS (LRA)

Analyze a linear range verification check standard quarterly (every 3 calendar months) for each TAL element and biennially for each non-TAL element.

The analytically determined concentration of this standard must be within ±5% of the true value. This concentration is the upper limit of the ICP linear range.

5.7 SERIAL DILUTION

Serial dilution is required for all samples analyzed on the ARL ICP Unit 2 at a frequency of one per ten samples. A 5x dilution should be used and all analyte results above the reporting limit on the diluted sample should agree with the original analysis within 10%. Otherwise, flag the result as estimated due to matrix interference.

6.0 INTERFERENCES

6.1 The aqueous digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

6.2 Soil/sediment/sludge samples are diverse and complex matrices. Both the LCS and the matrix spike samples are analyzed to evaluate the acid digestion procedure's effectiveness for a given waste type.

6.3 Glassware must be scrupulously clean to prevent cross contamination at trace levels. Griffin beakers should be replaced periodically as they tend to etch and hold traces of contamination.

6.4 Borosilicate glassware can cause contamination of boron, silicon, and sodium. Use Teflon beakers and lids to prevent this interference when these analytes are requested.

6.5 Spectral interferences can be categorized as (1) overlap of a target spectral line by a line from another element, (2) unresolved overlap of molecular band spectra, (3) background contribution from continuous or recombination phenomena, and (4) background contribution from stray light from the line emission of high concentration elements.

6.6 Physical interferences are generally associated with the sample nebulization and transport processes. Change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. A peristaltic pump may lessen these interferences. These types of interferences are operative and can be reduced by

sample dilution, use of an internal standard, and/or utilization of standard addition techniques.

High dissolved solids can cause salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution can control this problem. Control of the argon flow by the use of mass flow controllers improves instrument performance.

6.7 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. They can be minimized by careful selection of operating conditions (i.e., incident power, observation position, etc.), buffering the sample, matrix matching and standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte.

7.0 SAFETY PRECAUTIONS

7.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard.

7.2 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

7.2.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.2.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.3 Handle and store all reagents in accordance with the precautions listed on the Material Safety Data Sheets (MSDS).

7.3.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.3.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.3.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.4 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.5 Handle all glass equipment with care.

7.6 Perform acid digestions under an operating fume hood.

7.7 When preparing diluted solutions of concentrated acids, always add acid to water.

7.8 Tinted glass surrounding the plasma torch shields the intense ultraviolet light that is emitted. Also, heed warning labels on torch box: shut off power before opening door to torch box.

8.0 APPARATUS AND MATERIALS

8.1 Griffin beakers: 150-mL capacity, or equivalent glassware.

Note: Beakers will tend to etch over time and should be replaced periodically.

8.2 Watch glasses: ribbed and plain, or similar covers.

8.3 Fluted Teflon beakers with Teflon covers: 150-mL capacity.

8.4 Pipets: Volumetric class A, assorted sizes.

8.5 Filter Paper: Whatman #41.

8.6 Filter funnels.

8.7 Graduated cylinders: 100-mL capacity. Verify that the volumetric accuracy is within 2% upon receipt of new graduates.

8.8 Volumetric flasks: 100-mL, class A.

8.9 Hot plates: Thermolyne, Lindberg, or equivalent.

8.10 Fiberglass mat.

8.11 Inductively Coupled Plasma-Atomic Emission Spectrometer:

8.11.1 **ARL Model 3560** - simultaneous computer-controlled inductively coupled plasma - atomic emission spectrometer with background correction. Both units 1 and 2 are this make and model.

8.11.2 **Radio frequency generator.**

8.12 Argon gas: welding grade or better.

9.0 REAGENTS

9.1 Reagent water: Deionized water passed through a Barnstead Ultrapure Mixed Bed Cartridge or equivalent.

9.2 Acids: Ultra-high purity grade or equivalent.

9.2.1 **Hydrochloric acid** - concentrated, trace metals grade.

9.2.2 **Hydrochloric acid (1:1)** - Add 500 mL conc. HCl to 400 mL reagent water and dilute to volume with reagent water in a 1-L volumetric flask.

9.2.3 **Nitric acid** - concentrated, trace metals grade.

9.2.4 **Nitric acid (1:1)** - Add 500 mL conc. HNO_3 to 400 mL reagent water and dilute to volume with reagent water in a 1-L volumetric flask.

9.3 Stock standards for each analyte metal: purchased commercially. Standards must be suitable for ICP analysis and traceable to NIST standards.

Matrix spikes and laboratory control samples, as identified in Section 5.0, are prepared by spiking 0.50 mL of the following solutions, as necessary for the appropriate analytes, into 100-mL sample or reagent water aliquots.

9.3.1 **ICP Spiking Cocktails:** purchased premade from High Purity, or equivalent. All cocktails are 5% HCl by volume. See Table 1 for concentrations.

a. ICP A: Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Na, Ni, Zn, Si, Sr, V, W, Zn

b. ICP B: Ca, K, Mg, Pb, Se, Tl

c. ICP C: Mo, Sb, Sn, Ti

9.3.2 **ICP Silver Standard:** a 10 ppm working standard for silver is prepared by diluting 2.0 mL of a 1000 ppm stock silver standard to 200 mL in a volumetric flask with 2% HNO_3. The working standard is transferred to a clean, brown glass bottle, labeled and dated. This working standard expires in 1 month.

Note: Pipettes are NOT to be inserted into either the stock silver standard or the working standard. To obtain aliquots, pour small amounts of the standard into separate disposable cups and pipet aliquots from these cups. Discard any excess standard remaining in the disposable cups. DO NOT RETURN EXCESS to original standard container.

9.4 Mixed calibration standard solutions: Prepare two sets of mixed calibration standard solutions at three concentrations by combining appropriate volumes of the stock solutions, listed below, in volumetric flasks. Add (1:1) HNO_3 and (1:1) HCl to achieve a 1% HNO_3 and 5% HCl final solution. Dilute to volume with reagent water. Follow NUS Laboratory Procedure AP-006, Preparation of Inorganic Chemistry Standards.

9.4.1 **Mixed calibration standard solution #1** - includes the following elements at the corresponding concentrations (in mg/L):

- B, Ba, Be, Ca, Cd, Co, Cr, Mn, Mo, Ni. Pb, V, Zn: 1.0, 12.5, 25.0
- A, Ca, Fe, Mg, Na, K, Sn: 1.0, 125, 250
- Ag: 0.1, 0.5, 1.0

9.4.2 **Mixed calibration standard solution #2** - includes the following elements at the corresponding concentrations (in mg/L):

- As, Se, Sb, Tl: 1.0, 12.5, 25.0

9.5 Calibration blank: Prepare by diluting 2 mL of (1:1) HNO_3 and 10 mL of (1:1) HCl to 100 mL with reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

9.6 Continuing calibration standard (CCS): Prepare by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves.

9.7 Interference check sample (ICS): Laboratory-prepared or obtained from EPA, if available.

If true values for analytes contained in the ICS are not supplied with the ICS, determine the mean by initially analyzing the ICS at least five times repetitively for the particular analytes. Perform this mean determination during an analytical run where the results for the previously supplied EPA ICS met all recovery specifications. Additionally, use the result of this initial mean determination as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available commercially, prepare independent ICP Check Samples with interferant and analyte concentrations at the levels specified in Table 3 - Interferant and Analyte Elemental Concentrations Used for ICP Interference Check Sample. Establish the mean value and standard deviation by initially analyzing the Check Samples at least five times repetitively for each parameter on Table 3. Results must fall within the control limit of $\pm 20\%$ of the established mean value. Report the mean and standard deviation in the raw data.

Prepare the initial calibration verification (ICV) in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. This standard is independent of the calibration standards.

10.0 REFERENCES

10.1 "Methods for Chemical Analyses of Water and Wastes," U.S. EPA, Method 3005 & 200.7, 1979, Revised March 1983.

10.2 "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," U.S. EPA SW-846, Method 3050 A & 6010 A, July 1992.

10.3 Documentation Instrument 3560-5571 (2 volumes).

10.4 Plasma Vision Software Guide.

TABLE 1
WAVELENGTHS, REPORTING LIMITS, AND LINEAR RANGE

Element	Wavelength (nm)	Reporting Limit (μg/L)[1,2]	Linear Range (mg/L)
Aluminum	308.220	100	250
Antimony	206.840	200	250
Arsenic	193.700	100	250
Barium	455.400	5	50
Beryllium	313.040	5	50
Boron	249.770	50	*
Cadmium	226.500	5	250
Calcium	317.930	100	1000
Chromium	267.720	10	100
Cobalt	228.620	10	250
Copper	324.750	10	100
Iron	259.940	20	500
Lead	220.350	50	500
Lithium	670.780	5	*
Magnesium	279.080	50	250
Manganese	257.610	5	100
Molybdenum	202.030	50	*
Nickel	231.600	20	500
Potassium	766.490	200	250
Selenium	203.980	100	100
Silicon	251.610	50	*
Silver	328.070	10	25
Sodium	589.000	100	250
Strontium	407.770	10	*
Thallium	190.860	100	250
Tin	189.990	100	*
Titanium	337.280	10	*
Tungsten	239.710	100	*
Vanadium	292.400	10	500
Zinc	213.860	10	100
Zirconium	343.820	10	*

[1] Instrument detection limits (IDLs) are determined periodically and are published in memo form. Reporting limits are $\geq$ the IDLs.

[2] Reporting limit for soils (mg/kg) is obtained by dividing the reporting limit in μg/L by 10.

* Non-CLP element: the linear range only extends to the highest standard.

TABLE 2
ICP ANALYSIS SEQUENCE

Run #	Sample	Key
Instrument warmup and stabilization		
Initial calibration:		
1	ISB	ISB = internal standard blank
2	CB	CB = calibration blank
3	S1-1	S1-1 and S1-2 = low conc. calibration standard
4	S1-2	
5	S2-1	S2-1 and S2-2 = middle conc. calibration standard
6	S2-2	
7	S3-1	S3-1 and S3-2 = high conc. calibration standard
8	S3-2	
Initial QC checks:		
9	S3	
10	ICV-1	ICV-1 and ICV-2 = initial calibration verification
11	ICV-2	
12	ICB	ICB = initial calibration blank
13	RL	RL = reporting limit standard
14	ICS-A	ICS-A = interference check sample analytes only
15	ICS-AB	ICS-AB = interference check sample analytes and interferants
Sample analysis:		
16	SX1	SX = digestate: includes field samples, DUPs, MSs, prep blanks, LCSs
17	SX2	
18	SX3	
19	SX4	
20	SX5	
21	SX6	
22	SX7	
23	SX8	
24	SX9	
25	SX10	
Continuing QC checks:		
26	CCS-1	CCS-1 and CCS-2 = continuing calibration standards
27	CCS-2	
28	CCB	CCB = continuing calibration blank

Repeat sample analysis and continuing QC checks until all samples are analyzed.

Final QC checks:		
n-4	CCS-1	
n-3	CCS-2	
n-2	CCB	
n-1	ICS A	
n	ICS AB	n = last sequence number in run

TABLE 3
INTERFERANT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	Concentration (mg/L)	Interferants	Concentration (mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

TABLE 4
LAB CONTROL SAMPLE (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
WATER MATRICES - INSTRUMENT 3560
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L05W, Aluminum	AB21	Range: ---- RPD: ≤2.99%	Range: ≤2X IDL RPD: ≤3.93%	-----	-----	-----	94.9-106	92.2-108	100.34	2.70	1.19	94.8-105	92.1-108	99.97	2.61
				1.11	0.94	3.15									
L05W, Barium	AA38	Range: ---- RPD: ≤4.81%	Range: ≤2X IDL RPD: ≤6.60%	-----	-----	-----	95.2-101	93.7-102	98.06	1.45	1.85	95.2-100	94.0-101	97.71	1.24
				1.23	1.79	1.63									
L05W, Beryllium	AA39*	Range: ---- RPD: ----	Range: ≤2X IDL RPD: ≤20%	-----	-----	-----	97.5-106	95.3-109	101.92	2.20	1.22	91.1-107	87.2-111	99.00	3.93
				-----	-----	-----									
L05W, Cadmium	AA41	Range: ---- RPD: ----	Range: ≤2X IDL RPD: ≤20%	-----	-----	-----	88.2-113	82.0-119	100.45	6.14	0.52	82.1-111	74.8-119	96.67	7.30
				-----	-----	-----									
L05W, Calcium	AA43	Range: ---- RPD: ≤3.17%	Range: ≤2X IDL RPD: ≤4.26%	-----	-----	-----	94.1-103	91.9-105	98.39	2.17	1.29	72.0-135	56.2-151	103.73	15.84
				0.99	1.09	2.76									
L05W, Chromium	AA45	Range: ---- RPD: ----	Range: ≤2X IDL RPD: ≤20%	-----	-----	-----	90.1-110	85.2-114	99.82	4.86	0.67	88.4-107	83.7-112	97.88	4.73
				-----	-----	-----									
L05W, Cobalt	AA46	Range: ---- RPD: ----	Range: ≤2X IDL RPD: ≤20%	-----	-----	-----	97.7-107	95.4-109	102.34	2.33	1.10	90.4-106	86.4-110	98.26	3.94
				-----	-----	-----									
L05W, Copper	AA47	Range: ---- RPD: ----	Range: ≤2X IDL RPD: ≤20%	-----	-----	-----	96.2-104	94.2-106	100.34	2.05	1.57	94.0-102	92.0-104	97.93	1.97
				-----	-----	-----									
L05W, Iron	AA49	Range: ---- RPD: ≤3.88%	Range: ≤2X IDL RPD: ≤5.13%	-----	-----	-----	97.2-106	94.9-108	101.64	2.24	1.24	89.0-109	84.0-114	98.91	4.98
				1.38	1.25	2.30									
L05W, Magnesium	AB03	Range: --- RPD: ≤1.57%	Range: ≤2X IDL RPD: ≤2.06%	-----	-----	-----	96.4-103	94.8-104	99.55	1.58	2.01	91.4-105	87.9-109	98.29	3.47
				0.59	0.49	6.40									
L05W, Manganese	AB05	Range: ---- RPD: ≤2.54%	Range: ≤2X IDL RPD: ≤3.40%	-----	-----	-----	97.4-104	95.7-106	100.66	1.64	1.90	92.6-104	89.7-107	98.42	2.89
				0.82	0.86	3.56									
L05W, Nickel	AB07	Range: ---- RPD: ≤4.40%	Range: ≤2X IDL RPD: ≤5.87%	-----	-----	-----	95.6-108	92.5-111	101.85	3.10	0.88	90.8-108	86.6-112	99.21	4.19
				1.46	1.47	1.94									
L05W, Potassium	AB08	Range: --- RPD: ≤3.01%	Range: ≤2X IDL RPD: ≤3.93%	-----	-----	-----	90.8-103	87.8-106	96.73	2.99	0.75	90.8-111	85.8-116	100.89	5.05
				1.17	0.92	3.20									
L05W, Silver	AB49	Range: ____ RPD: ---	Range: ≤2X IDL RPD: ≤20%	-----	-----	-----	81.2-134	68.0-147	107.46	13.14	0.06	81.8-134	68.8-147	107.87	13.03
				-----	-----	-----									

TABLE 4 (CONT'D)
LAB CONTROL SAMPLE (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
WATER MATRICES - INSTRUMENT 3560
NOVEMBER 1993
(Continued)

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L05W, Sodium	AB10	Range: ---- RPD: ≤2.81%	Range: ≤2X IDL RPD: ≤2.79%	---------- 0.96	---- 0.61	------ 4.94	94.3-103	92.3-105	98.48	2.07	1.37	87.3-109	81.9-114	98.08	5.39
L05W, Vanadium	AB13*	Range: ---- RPD: ----	Range: ≤2X IDL RPD: ≤20%	---------- ----------	---- ----	------ ------	95.2-99.9	94.0-101	97.56	1.18	2.14	91.4-102	88.6-105	96.92	2.78
L05W, Zinc	AB14	Range: ---- RPD: ≤6.01%	Range: ≤2X IDL RPD: ≤8.19%	---------- 1.65	---- 2.18	------ 1.28	94.2-103	92.0-105	98.70	2.24	1.29	86.8-106	82.1-110	96.20	4.71

PM = preparation method
x = mean
s = standard deviation
CI = confidence interval
LCS = lab control standard
IDL = instrument detection limit
[1] Cpk based on 10% RPD specification goal.
[2] Cpk based on 90-110% recovery specification goal.

TABLE 4 (CONT'D)
LAB CONTROL SAMPLE (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
SOLID MATRICES - INSTRUMENT 3560
November 1993

PM, Analyte	Comb. ID.	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[2]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L03S, Aluminum	BB08	Range: --- RPD: ___	Range: <4X IDL RPD: ≤40%	--------- ---------	---- ----	----- -----	62.0-167	52.9-153	114.47	26.21	0.13	7.8-229	0-284	118.38	55.29
L03S, Barium	BB14	Range: --- RPD: ≤24.4%	Range: <4X IDL RPD: ≤33.0%	--------- 7.41	---- 8.52	----- 0.49	79.4-107	69.4-136	93.43	7.02	0.88	82.1-114	74.1-122	98.24	8.05
L03S, Beryllium	BB15	Range: --- RPD: ___	Range: <4X IDL RPD: ≤40%	--------- ---------	---- ----	----- -----	78.2-104	63.7-139	91.35	6.57	0.83	86.1-113	79.5-119	99.44	6.65
L03S, Cadmium	BB18	Range: --- RPD: ≤25.3%	Range: <4X IDL RPD: ≤33.8%	--------- 8.25	---- 8.53	----- 0.46	81.3-106	58.4-140	93.84	6.29	1.00	60.4-114	47.0-128	87.34	13.46
L03S, Calcium	BB19	Range: --- RPD: ___	Range: <4X IDL RPD: ≤40%	--------- ---------	---- ----	----- -----	70.7-109	67.8-136	89.60	9.46	0.51	61.9-124	46.4-140	93.03	15.55
L03S, Chromium	BB21	Range: --- RPD: ≤20.7%	Range: <4X IDL RPD: ≤27.7%	--------- 6.74	---- 6.98	----- 0.63	76.8-112	59.0-138	94.41	8.81	0.73	58.2-164	31.7-191	111.28	26.52
L03S, Cobalt	BB22	Range: --- RPD: ≤26.6%	Range: <4X IDL RPD: ≤35.9%	--------- 7.90	---- 9.33	----- 0.43	81.7-119	63.3-139	100.47	9.38	0.87	72.8-122	60.4-135	97.59	12.40
L03S, Copper	BB24	Range: --- RPD: ≤23.0%	Range: <4X IDL RPD: ≤31.2%	--------- 6.41	---- 8.27	----- 0.55	83.2-106	61.5-141	94.72	5.79	1.14	76.3-123	64.6-134	99.49	11.62
L03S, Iron	BB26	Range: --- RPD: ___	Range: <4X IDL RPD: ≤40%	--------- ---------	---- ----	----- -----	73.6-125	67.0-150	99.38	12.89	0.63	27.5-249	0-305	138.36	55.41
L03S, Magnesium	BB06	Range: --- RPD: ≤15.9%	Range: <4X IDL RPD: ≤21.6%	--------- 4.55	---- 5.68	----- 0.91	76.6-107	63.1-141	92.01	7.69	0.74	33.1-181	0-218	107.20	37.03
L03S, Manganese	BA28	Range: --- RPD: ≤44.4%	Range: <4X IDL RPD: ≤56.3%	--------- 20.69	---- 11.87	----- 0.02	83.9-108	68.8-135	95.83	5.98	1.16	62.1-123	47.0-138	92.35	15.13
L03S, Nickel	BA32	Range: --- RPD: ≤57.3%	Range: <4X IDL RPD: ≤76.4%	--------- 19.29	---- 19.02	----- 0.01	83.9-108	59.1-143	95.76	5.93	1.17	73.7-115	63.3-126	94.41	10.37
L03S, Potassium	BA33	Range: --- RPD: ___	Range: <4X IDL RPD: ≤40%	--------- ---------	---- ----	----- -----	69.3-128	63.1-133	98.55	14.62	0.54	76.9-117	66.8-127	97.03	10.08
L03S, Silver	BA36	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--------- ---------	---- ----	----- -----	80.4-122	40.4-146	101.23	10.39	0.76	49.1-147	24.6-172	98.04	24.47

TABLE 4 (CONT'D)
LAB CONTROL SAMPLE (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
SOLID MATRICES - INSTRUMENT 3560
NOVEMBER 1993
(Continued)

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x̄	s	RPD Cpk[2]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x̄	s	LCS Cpk[3]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x̄	s
L03S, Sodium	BA37	Range: --- RPD ____	Range: <4X IDL RPD: ≤40%	--------- ---------	----- -----	------ ------	75.2-114	52.0-146	94.74	9.78	0.67	78.4-123	67.2-134	100.81	11.19
L03S, Vanadium	BA40	Range: --- RPD ____	Range: <4X IDL RPD: ≤40%	--------- ---------	----- -----	------ ------	80.3-116	67.5-136	97.95	8.84	0.87	83.8-120	74.7-129	101.90	9.07
L03S, Zinc	BA42	Range: --- RPD: ≤49.4%	Range: <4X IDL RPD: ≤61.5%	--------- 25.13	----- 12.12	------ 0.14	76.6-102	57.5-152	89.17	6.27	0.75	60.4-125	44.2-141	92.72	16.17

PM = preparation method
x̄ = mean
s = standard deviation

LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit

[2] Cpk based on 20% RPD goal.

[3] Cpk based on 75-125% recovery goal.

TABLE 5
SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS BY ICP

Element	Water/Soil (µg/L)
Aluminum	2,000
Antimony	5,000
Arsenic	5,000
Barium	2,000
Beryllium	50
Boron	5,000
Cadmium	50
Calcium	10,000
Chromium	200
Cobalt	500
Copper	250
Iron	1,000
Lead	500
Lithium	200
Magnesium	5,000
Manganese	500
Molybdenum	2,000
Nickel	500
Potassium	5,000
Selenium	5,000
Silicon	5,000
Silver	50
Sodium	10,000
Strontium	2,000
Thallium	10,000
Tin	2,000
Titanium	5,000
Tungsten	5,000
Vanadium	2,000
Zinc	500
Zirconium	5,000

[1] The levels shown indicate concentrations in the final digestate of the spiked sample (100-mL final volume).

FIGURE 1
STATUS PRINTOUT

Task : CLP 12:54 PM 22/ 7/92

Measurement Details

Pre-Integration Time	30
Off-Peak Integrations	1
On-Peak Integrations	2
Integration Time	5.0
Autosampler Rack Size	10
Forward Power	650 W
Reflected Power	<10 W
Auxilliary Gas Pressure	
Auxilliary Gas Flow	
Coolant Gas Pressure	
Coolant Gas Flow	
Carrier Gas Pressure	
Carrier Gas Flow	
Pump Speed	
Pump Tubing Rating	Y/Y

Analytical Lines

Report Name	Units	Channel	BG1	BG2	Order	Wavelength(nm)	Internal Std
Be	ppm	15	0	80	2	313.050	
Na	ppm	10	-60	0	1	589.000	
Mg	ppm	5	0	80	2	279.080	
Al	ppm	13	-80	0	2	308.220	
K	ppm	29	0	60	1	766.490	
Ca	ppm	16	0	80	2	317.930	
Y	ppm	9	-60	0	2	292.400	
Cr-	ppm	32	0	80	3	267.720	
Mn	ppm	30	-60	60	3	257.610	
Fe	ppm	31	0	80	3	259.940	
Co	ppm	24	-60	0	3	228.620	
Ni	ppm	25	-60	0	3	231.600	
Cu	ppm	18	-60	0	2	324.750	
Zn	ppm	17	0	80	3	213.860	
As	ppm	8	-45	45	3	193.700	
Se	ppm	12	0	60	3	203.980	
Li	ppm	21	0	80	1	670.780	
Ag	ppm	19	-80	0	2	328.070	
Cd	ppm	23	0	80	3	226.500	
Sb	ppm	14	-60	0	3	206.840	
Ba	ppm	4	0	80	1	455.400	
Tl	ppm	7	0	45	3	190.850	
Pb	ppm	20	-45	45	3	220.350	
B	ppm	27	0	80	3	249.770	
Si	ppm	28	-40	0	3	251.610	
Ti	ppm	22	0	80	2	337.280	
Sr	ppm	2	0	80	1	407.770	
Zr	ppm	1	0	80	1	343.820	
Mo	ppm	11	0	80	3	202.030	
Sn	ppm	6	-60	60	3	189.990	
W	ppm	26	0	80	3	239.710	

FIGURE 2
PROFILE CURVES

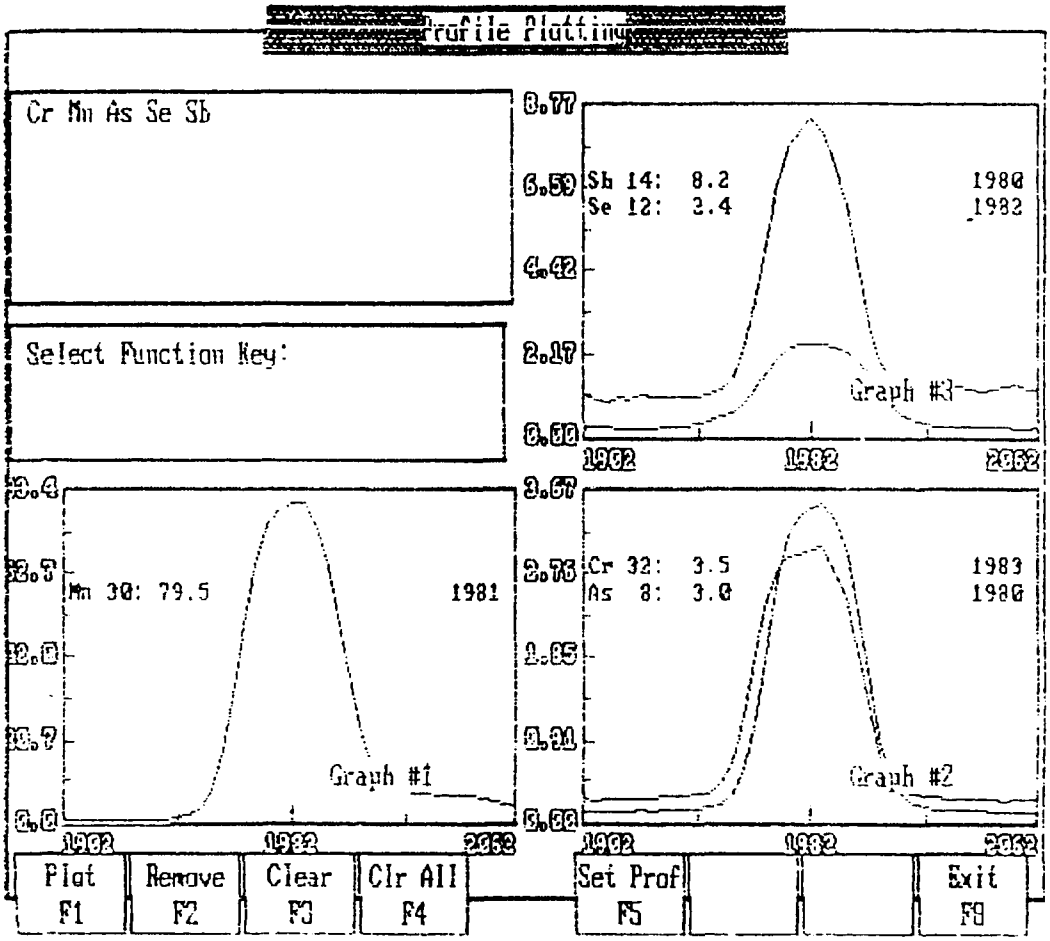

FIGURE 3
AUTO-REFIT CURVES PRINTOUT

Least Squares Regression Report
Analyte : Fe Channel : 31
Order : 1st Order
Weighting : Inverse Intensity Squared
Print Date :

Task Name : COPY
Internal Standard : Y

8:28 AM Tuesday March 22, 1994

Intercept : -1.625472E-03
Coefficient 2 : 1.356291E+02

Std	Concentration	Calc. Conc	% Delta Conc	Kpulses	%RSD Kpulses	I.S. Kounses	Used in Regression
1	0.0000	0.0000		0.001	0.0000	83.442	Included
2	1.0000	0.9978	0.2218	0.612	0.0009	85.122	Included
3	125.0000	124.8983	0.0814	71.687	0.0002	77.845	Included
4	250.0000	250.7598	-0.3039	139.997	0.0045	75.720	Included

Correlation Coefficient : 9.9999313E-01
Root Mean Square : 1.9245983E-01
Standard Error of Estimate : 3.8854198E-01

FIGURE 4
LOGBOOK PAGE

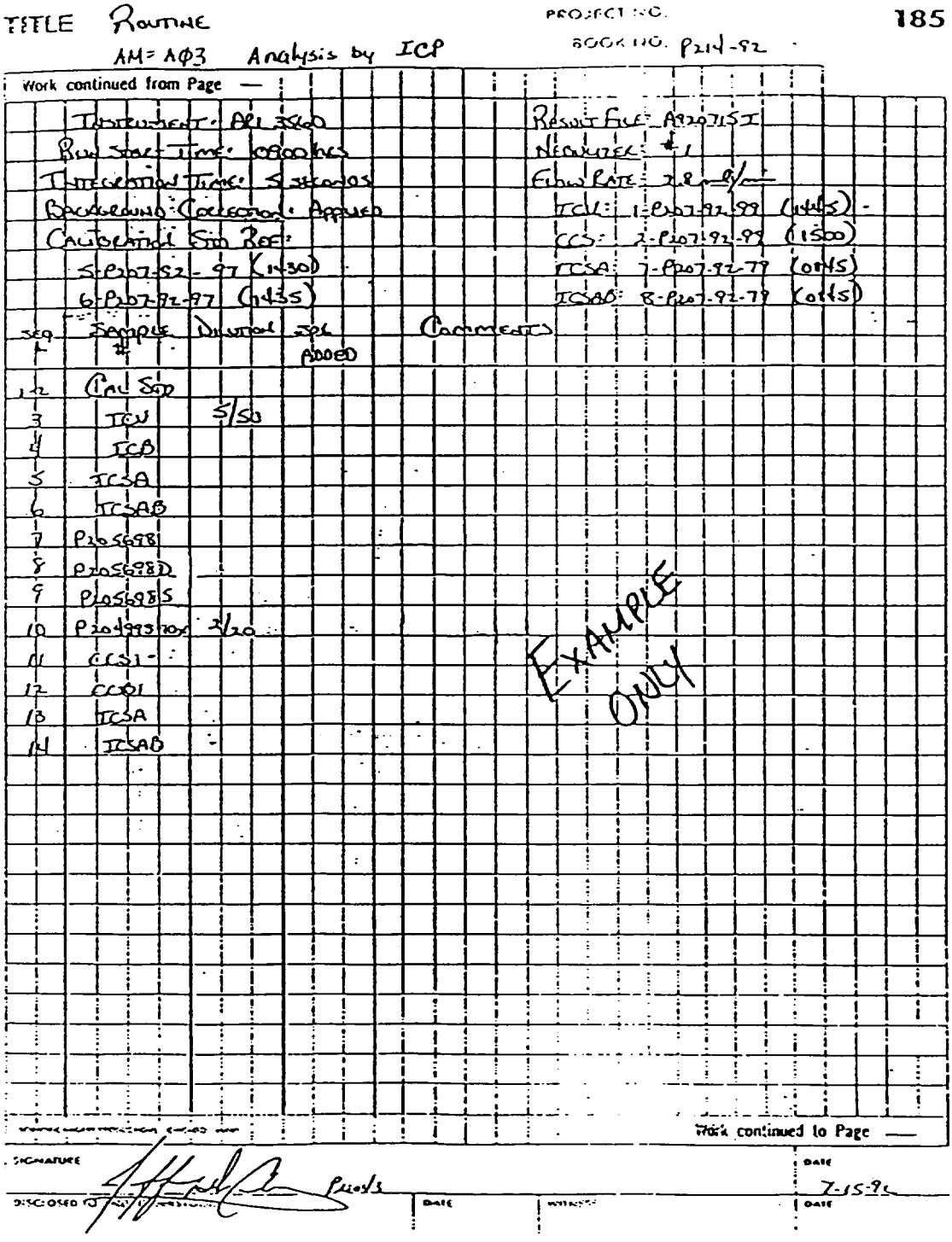

FIGURE 5
WORKSHEET ENTRIES

WORKSHEET
July 13, 1992
ICP

EXAMPLE ONLY

BATCH 11356 PM: L02V AM:

Sample	Type	Client	Date Sampled	Date Received	Date Due	Prep	Anls	Sample Description
204993	ORIG	-	J1-JUL-92	02-JUL-92	22-JUL-92	L02VFRZ-	AGSR-	YELLOW FOLDER FOUND IN #1

SAMPLE INSTRUCTIONS

Ref.	Analysis Date	Instrument	Anlst	Run Cup No.	Start Time	Run File	Comments
1	7-14-92	3560	21043	30	1528	A920714I	
2	7-15-92	↓	↓		0900	A920715I	
3							
4							
5							

Analyte	Type	Ref	Dilu.	Result	Unit	Book	Page	Range	RPD	MSR I Rec	TV/SA	Reviewed
Silver, Leachable (Ag)	ORIG	2	10	<0.1	mg/l	P214-92	185					EM

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LABORATORY METHOD

GRAPHITE FURNACE ATOMIC ABSORPTION

METHOD ID: CRA/SN-GFAA
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

GRAPHITE FURNACE ATOMIC ABSORPTION

1.0 SCOPE AND APPLICATION

Metals in solution are readily determined by atomic absorption spectroscopy. As opposed to conventional flame analysis, a greater percentage of available analyte atoms are vaporized and dissociated for absorption when the furnace technique is used. Additional advantages of this technique include the use of smaller sample volumes and the detection of lower concentrations of elements.

This method is applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes (see Table 1 for analytes and reporting limits). Drinking water, ground water, other aqueous samples, TCLP and EP extracts, industrial wastes, soils, sludges, sediments and other solid wastes require digestion prior to analysis.

This method is specific to the Perkin-Elmer 3030. The appendix includes information specific to the PE-5100 and the PE-4100.

2.0 SUMMARY OF METHOD

A mixture of sample is acid digested on a hot plate and evaporated to a low volume. The digestate is cooled, filtered if necessary, and brought to final volume with reagent water.

A small aliquot of a sample digestate is placed into the graphite tube in the furnace. The digestate is then treated thermally. First, a low current heats the tube to evaporate the sample to dryness. Then at a higher temperature to destroy organic matter and volatilize other matrix components. Finally, the tube is heated to incandescence which, in an inert atmosphere, atomizes the element being determined, forming a ground-state vapor. Radiation from a hollow cathode lamp or electrodeless discharge lamp, characteristic of the metal analyte, passes through the ground-state vapor. A photoelectric detector measures the intensity of transmitted radiation which decreases in proportion to the concentration of metal analyte in the sample.

3.0 GRAPHITE FURNACE PROCEDURE (PE-3030)

Note: See Appendix to this procedure for operation of the PE-5100 and PE-4100.

Approvals:

Charles A Kiely	4/12/94	Jonetta Talbott	4/12/94		4/12/94
Technical Operations Manager	Date	Group Leader	Date	Quality Assurance Director	Date

3.1 SAMPLE PRESERVATION

3.1.1 Store all water samples in either plastic or glass bottles preseved with nitric acid (to pH <2). Samples must be analyzed within six months.

3.1.2 Store all soil samples upreserved in either plastic or glass containers. Samples must be analyzed within six months.

3.2 SAMPLE PREPARATION

3.2.1 Hot Plate Acid Digestion of Water Samples for Total Metals Determination

a. Turn on the fume hoods and ensure that there is adequate air ventilation. Turn on hot plates to allow them to achieve initial digestion/evaporation temperature while samples are being prepared for digestion. Set Thermolyne hot plates at approximately 5 and Lindberg hot plates to 5.5 - 6.0.

b. Shake the sample bottle vigorously to achieve homogeneity. Immediately transfer 100 mL of the sample to a 150-mL Griffin beaker using a graduated cylinder.

c. Add 3 mL of concentrated nitric acid (HNO_3) and cover with a ribbed watch glass or similar device.

d. Place beaker on the hot plate in the hood and cautiously evaporate the sample to a volume of approximately 5 mL.

During evaporation, ensure that the sample does not boil and that no portion of the bottom of the beaker goes dry. If the sample goes to dryness, discard the sample and reprepare.

e. Allow the digestate to cool then add another 3-mL volume of concentrated HNO_3. Cover the beaker with a plain watch glass and place it on the hot plate. Increase the hot plate temperature if necessary to obtain a gentle reflux action. Reflux for 30 minutes.

f. Cool the beaker and add 10 mL of reagent water. Cover with the plain watch glass and gently warm the beaker for 15 minutes. Ensure that any precipitate is dissolved while warming.

g. Cool the beaker. Rinse the watch glass with reagent water, collecting the washings in the beaker. Rinse the walls of the beaker with reagent water.

h. If visible solids are observed in any one of the samples in a batch, filter all digestates within that batch, including the associated quality control samples as outlined below. Otherwise, proceed to 3.2.1.i.

h.1 Assemble a filter funnel and Whatman #41 filter paper. Prerinse the filter/funnel apparatus with 1% HNO_3 solution.

h.2 Place a 100-mL volumetric flask under the funnel. Quantitatively transfer the contents of the beaker into the prerinsed filter/funnel apparatus with reagent water.

h.3 Rinse the filter paper thoroughly with reagent water. Rinse the tip of the funnel, collecting the washings in the volumetric flask. Proceed to 3.2.1.j.

i. If none of the digestates require filtration, quantitatively transfer the digestate to a 100-mL volumetric flask.

j. Bring the digestate to volume with reagent water and mix thoroughly by inversion.

k. Transfer the digestate to a prelabeled polyethylene bottle with a polyethylene-lined cap.

Obtain labels for sample bottles by using LIMS program ALABEL. This program prints labels, by sample batch, which lists the unique NUS Laboratory sample number, client, batch number, sample type (LCS, dup, orig), preparation description, date of preparation, and initial/final volumes.

3.2.2 Hot Plate Acid Digestion of Solid Samples for Total Metals Determination

a. Turn on the fume hoods and ensure that there is adequate air ventilation. Turn on hot plates to allow them to achieve initial digestion/evaporation temperature while samples are being prepared for digestion. Set Thermolyne hot plates at approximately 5 and Lindberg hot plates to 5.5 - 6.0.

b. Mix the sample to achieve homogeneity. Weigh a 1.00 ±0.01 g (wet weight) aliquot of sample into a 150-mL Griffing beaker. Record the weight to the nearest 0.01 g.

c. Add 10 mL of 1:1 nitric acid (HNO_3). Mix the sample to a slurry consistency and cover with a plain watch glass.

d. Place the beaker on the hot plate in the hood and cautiously reflux the sample for 15 minutes without boiling.

e. Allow the digestate to cool. Rinse the watchglass with a minimum of reagent water, collecting the rinsate in the beaker. Then add 5 mL of concentrated HNO_3. Place the beaker on the hot plate and reflux for 30 min.

f. Repeat step 3.2.2.e to complete the oxidation process.

g. Using a ribbed watch glass, place beaker on the hot plate in the hood and cautiously evaporate the sample to a volume of approximately 5 mL.

During evaporation, ensure that the sample does not boil and that no portion of the bottom of the beaker goes dry. If the sample goes to dryness, discard the sample and reprepare.

h. Cool the beaker and add 2 mL of reagent water and 2.5 mL of 30% hydrogen peroxide. Cover the beaker with the plain watch glass and gently warm the beaker to start the peroxide reaction. Heat until effervescence ceases, then cool the beaker.

CAUTION: Hydrogen peroxide may react vigorously. Care must be taken to avoid sample losses due to splattering during peroxide reaction.

i. Add 30% hydrogen peroxide in additional 2.5-mL aliquots with gentle warming until effervescence is minimal or until no change is observed in the sample's appearance. Do not add more than a total of 10 mL of 30% hydrogen peroxide to any one sample.

j. Cover the beaker with a ribbed watch glass and reduce the volume of the digestate to approximately 5 mL on the hot plate. Maintain a covering of solution on the bottom of the beaker. If any part of the sample goes to dryness, discard the sample and reprepare. DO NOT BOIL.

k. Cool the beaker. Rinse the watch glass with a mimimum of reagent water, collecting the washings in the beaker. Rinse the sides of the beaker with reagent water.

l. Filter all digestates, including the associated quality control samples, as outlined above in Section 3.2.1.h.

m. Transfer the digestate to a prelabeled polyethylene bottle with a polyethylene-lined cap.

Obtain labels for sample bottles by using LIMS program ALABEL. This program prints labels, by sample batch, which lists the unique NUS Laboratory sample number, client, batch number, sample type (LCS, dup, orig), preparation description, date of preparation and initial/final volumes.

3.3 PRELIMINARY SET-UP

Note: The PE-3030 has two kinds of command keys: hard keys, whose functions do not change, and soft keys, whose functions change from mode to mode and from entry to entry within each mode. The current function for each soft key is displayed on the screen directly above the key. In this procedure, **HARD KEYS** are indicated with bold capitals and

[SOFT KEYS] are indicated with bracketed capitals.

3.3.1 Turn on argon gas (48-55 psi).

3.3.2 Turn on the recirculator (two buttons: temperature and pump).

a. Verify temperature is set in a range of 5-10°C.

b. Set temperature, if necessary, by turning the temperature dial while holding down the temperature button.

3.3.3 Turn on the following equipment:

- HGA-600 unit.
- Zeeman background correction unit.
- PE-3030 main instrument.
- Printer. Also, verify that the printer is on-line.

3.3.4 Check that rinse solution is filled and that the waste container is empty.

3.4 ELEMENT PROGRAM SELECTION

Note: The User disk is kept in the PE-3030's disk drive and should not be removed.

3.4.1 Press **USER INDEX**. This calls up the main menu from the disk.

3.4.2 Choose the element of interest from the menu. Type in the element number then press **RECALL**. This loads the selected element file which includes the specific slit width and wavelength to be used.

3.4.3 Adjust the slit width and the analytical wavelength using the manual controls knobs.

Note: Residential well analyses of Sb must be performed on the PE-5100; see the Appendix for details.

3.5 LAMP INSTALLATION AND ALIGNMENT

3.5.1 Select and install the proper lamp for the appropriate element from Table 2A. Proceed with either 3.3.1 a or b depending upon the lamp type as identified in the table.

a. Hollow Cathode Lamp (HC)

a.1 Raise the lamp compartment cover on the 3030.

a.2 Press **PROG**. Verify that the lamp current is set to zero before installing the HC.

a.3 Plug the lamp connector cable into one of the power supply sockets.

a.4 Install lamp into the turret location corresponding to the number on the power socket so that lamp is approximately centered with the window facing the Zeeman furnace.

a.5 Type in proper lamp current from Table 2A.

a.6 Allow the lamp to warm up for a minimum of 5 minutes.

b. Electrodeless Discharge Lamp (EDL)

b.1 Raise the lamp compartment cover on the 3030.

b.2 Verify that lamp current knob is turned off and that the EXT MOD/CONTINUOUS switch at the rear of the EDL power supply is set at CONTINUOUS. If not, set them as such.

b.3 Connect the EDL cables to the EDL power supply cables.

b.4 Turn on the EDL Power Supply. Also turn on the lamp current knob.

b.5 Light the EDL manually by passing another light source near the EDL window.

b.6 Install the lamp so that it is approximately centered with the window facing the Zeeman furnace.

b.7 Set energy level listed in Table 2A by adjusting current knob on the EDL Power Supply.

b.8 Allow the lamp to warm up for a minimum of 30 minutes.

3.5.2 Press **SET UP** after the lamp has warmed up. Adjust the lamp position to maximize the energy as indicated by the bar graph on the monitor. Press **GAIN** to return the bar graph to an optimum, mid-range level. Adjust the alignment screws and slide the lamp in and out to maximize the energy reading.

3.6 FURNACE SET-UP

3.6.1 Press the **FURNACE** button on the Perkin-Elmer HGA-600. This will open the furnace chamber.

3.6.2 Remove the graphite tube. Clean the furnace area, including the two

windows and contact cylinders, with a cotton swab and isopropyl alcohol.

3.6.3 Check the tube for signs of corrosion and/or flaking. If these signs are present, replace tube.

Note: It is good practice to replace the tube every day of analysis.

3.6.4 Select the appropriate tube type from Table 2. When PG is specified (as is the case for all but Sn, V, and Mo analyses), load a L'vov platform into a new tube as follows:

a. Hold the graphite tube horizontally so that the groves are at the bottom and the sample introduction hole is at the top.

b. Slide the platform partially into the grooves in the graphite tube.

c. Press down on the insertion tool while pushing the platform into place. When the platform is correctly inserted it will remain in position when the tube is turned upside down and gently shaken.

3.6.5 Insert and align the graphite tube into the furnace.

a. Insert the tube into the contact cylinder, so that the sample introduction hole in the tube lines up approximately with the sample port.

Note: Make certain that the tube end with the grooves is at the left, otherwise the sample will be dispensed onto the wall of the tube and not into the cavity of the platform.

b. Insert the tube alignment tool into the sample port. carefully move and turn the graphite tube until the tip of the tool goes into the sample introduction hole in the tube. Do not remove the tool.

c. Close the furnace by pressing **FURNACE**, then remove the tool.

3.6.6 Condition a new graphite tube, or clean a previously used tube, with a high temperature burn as follows:

a. Press **RUN** then press [HGA ON/OFF].

b. Continue dry firing the instrument until the tube is free from contamination.

3.7 SAMPLE/STANDARD LOADING

3.7.1 Prepare standard solutions. Document the preparation in GFAA Standards log book. Refer to Table 4 for standard concentrations, matrix modifiers, and calibration type for the element of interest.

3.7.2 Place sample digestions and prepared standard solutions linearly on bench in the order that they are to be loaded onto the autosampler and analyzed.

3.7.3 Prepare autosampler as follows:

a. Press [SAMPLER RESET]. This takes autosampler position to zero.

Note: Press this button once only. If this button is pushed during a run, the autosampler will reset and the run will be lost.

b. Pipette sample/standard into autosampler cup. Add matrix modifier, if necessary.

c. Load cups into autosampler tray. Verify autosampler loading as described in NUS Laboratory Procedure AP-013.

3.8 CALIBRATION AND ANALYSIS

3.8.1 Perform the analytical sequence as listed in Table 5. Perform a minimum of two replicate firings for standardization, QC and sample analyses. QC criteria are specified in Section 5.

3.8.2 Press **PROG**. This brings up the first programming mode page. Change the following three items:

a. Lamp current - enter numeric value from Table 2A (set to zero if using an EDL).

b. Printer - select SUPPL DATA for supplemental information.

c. Statistics - Select AVG. & SD & CV for the appropriate statistical evaluation.

3.8.3 Press **PROG** two more times. This brings up the third programming mode page. Change sample numbers to read "Sample 01 to 01". Press [ENTER]

3.8.4 Press the following sequence of keys: **RUN**, [CHECK], [SAMPLER ON/OFF], type "1" for starting cup number, **PRINT**. The instrument will analyze the calibration curve samples and then analyze the ICV (sample 01).

3.8.5 Verify that calibration is acceptable by averaging each set of replicate firings (ZAA values). Use a statistical calculator to find the correlation coefficient of these averages. If calibration is not acceptable, correct the problem and repeat calibration.

3.8.6 Press **DISP CALIB, PRINT SCRN**, then **PROG** twice, **PRINT SCRN**. This prints the necessary calibration and element program information.

3.8.7 Press **PROG** once more. Enter the final sample cup number in the field "Sample 01 to __".

3.8.8 Press the following sequence of keys: **RUN**, [CHECK], "2" (for starting cup number), [SAMPLER ON/OFF]. The instrument will analyze all of the samples in the autosampler.

Note: It is important to document the sample numbers, in sequence, at the start of the run. The computer print-out does not contain the NUS Laboratory sample numbers.

3.8.9 When sample analyte concentration exceeds the concentration of the high standard, reanalyze the sample after appropriate dilution. Prepare sample dilutions with reagent water acidified with 1 mL of HNO_3 per 100 mL. Use the least dilution necessary to bring the analyte within the upper two thirds of the analytical range.

Note: Samples being analyzed for Sb and Sn must be diluted with reagent water acidified with 1 mL of HNO_3 and 5 mL HCl per 100 mL.

If the analytical spike of a sample exceeds the high standard while the sample result does not, and the analytical spike yields an acceptable recovery in the range of 85-115%, neither the sample nor the spike requires reanalysis at dilution.

3.8.10 When a low-level sample is analyzed immediately after a very high concentration sample, particularly for refractory metals, be aware of the possibility of carryover contamination. Recheck low-level positive results, as necessary, to ensure the absence of carryover.

3.9 INSTRUMENT SHUT-DOWN

3.9.1 Turn off lamp energy, either by adjusting the EDL Power Knob to zero (if using an EDL) or by pressing **PROG** and then entering zero at the lamp current prompt (if using an HC).

3.9.2 Turn off the PE-3030 main instrument, the Zeeman background correction unit, the HGA-600 unit, the printer and the EDL Power Supply (if used).

3.9.3 Turn off the recirculator, both buttons.

3.9.4 Leave the inert gases on unless the instrument is being shut down for an extended period of time.

3.9.5 Turn the EXT MOD/CONTINUOUS switch at the rear of the EDL power supply to CONTINUOUS.

3.10 CALCULATIONS

3.10.1 Read the metal value in mg/L (i.e., the average of the two firings) directly from the instrument printout.

3.10.2 For aqueous samples report metal concentrations in mg/L using the following equation:

$$Metal_{(mg/L)} = A \times \frac{FV}{IV}$$

where A = metal in mg/L of sample digestate from calibration curve
FV = final volume of dilution (=1 if no dilution)
IV = initial volume of sample (=1 if no dilution)

3.10.3 For solid samples report metal concentrations as mg/kg, wet or dry weight, using the equation(s) below:

a. Solid samples - wet weight:

$$Metal_{(mg/kg\ wet)} = \frac{A \times V}{W}$$

where A = metal in mg/L of sample digestate from calibration curve
V = final volume of sample digestate in mL
W = wet weight of sample in grams

b. Solid samples - dry weight:

$$Metal_{(mg/kg\ dry)} = Metal_{(mg/kg\ wet)} \times \frac{100}{\%\ solids}$$

4.0 DATA COLLECTION

4.1 Document the following information in a bound lab notebook for each set of acid digestions performed. Entries must be made at the time of digestion. An example logbook entry is shown in Figure 1 and briefly described below:

- preparation method (PM) code.
- date/time performed and analyst(s) signature(s)/employee number(s).
- NUS Laboratory sample number and aliquot. Identify any quality control samples (method blank, LCS, dup/MS).
- spiking standards, by standard identification number and volumes used.
- batch number.

4.2 Document all data in a bound lab notebook and on the printed worklist for each

set of analyses performed. Entries must be made at the time of analysis.

4.2.1 BOUND LABORATORY NOTEBOOK (see Figure 2)

Document the following:

- brief description of test and analyte.
- instrument number (e.g., PE-3030).
- standard reference number.
- matrix modifier, if any.
- sample aliquot.
- NUS Laboratory sample numbers with appropriate dilutions, spikes and comments, if any. Identify any lab quality control samples (method blanks, duplicates, MS/MSDs, LCSs, etc.).
- date/time analysis started and analyst(s) signature(s).

4.2.2 PRINTED WORKSHEET (see Figure 3)

Document the following:

- date/time analysis started and analyst(s) employee number(s).
- instrument number and run file.
- sample cup numbers and results, with units, taken from computer printout (see Figure 3).
- book and page reference to data in bound lab notebook.

4.3 Forward the following to data management from each analytical run:

- preparation raw data, including standards/spiking solutions preparation pages.
- analytical raw data, including logbook page(s), worksheet/assignment sheets, and instrument printouts.
- description of problems encountered and actions taken during sample preparation and analysis on corrective action records.
- initial and continuing calibration files from the instrument software system.
- sample and associated quality control sample files (method blanks, MS/MSDs, LCSs) from the instrument software system.

- any instrument maintenance documented in the instrument maintenance log.

5.0 QUALITY CONTROL

5.1 INSTRUMENT CONTROL CHECKS

5.1.1 Initial Calibration Verification (ICV)

Verify and document the accuracy of the initial calibration by analyzing an initial calibration verification standard, independent of the calibration standard, immediately after instrument calibration.

When measurements exceed the control limits of 90-110%, terminate analysis and correct the problem which may be due to instrument set-up or function and/or accuracy of the standard materials. Recalibrate the instrument and verify the calibration before proceeding with the analysis sequence.

5.1.2 Initial Calibration Blank (ICB)

Analyze an initial calibration blank immediately after the ICV.

If the absolute value of the blank result exceeds the reporting limit, terminate analysis, correct the problem, recalibrate, and verify the calibration.

5.1.3 Reporting Limit Standard

Analyze a standard at the reporting limit, following the ICB, to verify that the instrument has adequate sensitivity. The response for this standard must be discernible from the ICB; that is, it must yield a recovery at greater than 50%. If less than a 50% recovery is observed, repour and reanalyze the reporting limit standard and/or troubleshoot the analysis or calibration until the cause is corrected.

5.1.4 Continuing Calibration Standard (CCS)

Analyze a mid-range standard for continuing calibration, after each set of 10 analyses and at the end of each run, to ensure calibration accuracy during each run.

Recovery limits for CCS are 85.0-115% for routine analysis samples and 90.0-110% for NPDWR compliance monitoring and New Jersey samples. If CCS acceptance limits are not met, terminate analysis, correct the problem, recalibrate, and verify the calibration. Reanalyze all field and quality control samples analyze since the last acceptable ICV or CCS standard.

5.1.5 Continuing Calibration Blank (CCB)

Analyze a calibration blank after each CCS standard.

If the absolute value of the blank result exceeds the reporting limit, terminate analysis, correct the problem, recalibrate, and verify the calibration. Reanalyze all field and quality control samples analyzed since the last acceptable calibration blank.

5.1.6 Single Spike Analysis

Perform a single-point, post-digestion spike analysis on each field sample to check for sample matrix interference (the quality control sample may be excluded).

For most elements, spike post-digestion spikes at a concentration equal to the midpoint of the graphite furnace calibration curve for each element. Cadmium is spiked at 0.005 mg/L. Analyze the spike immediately following the original sample analysis.

Depending on the original sample result, follow a, b, or c to evaluate the single spike results.

Note: For the analysis of lead and selenium on drinking water samples, recovery of the analytical spike must be 85-115%. Recovery outside this range requires analysis by method of standard additions as outlined in Section 5.5.

a. The original sample yields a result less than two times the reporting limit:

a.1 If analytical spike recovery is between 85 and 115%, report the sample result.

a.2 If analytical spike recovery is between 50 and 85% or 115 and 150%, report the sample result correcting for the analytical spike recovery. Qualify the data with the following comment for that sample:

A single-point, post-digestion spike was performed on this sample analyte. The sample result is corrected for the recovery of the spike on this analyte.

a.3 If the analytical spike recovery is less than 50% or greater than 150%, dilute the sample by a factor of 2 to 5, depending upon the background correction and/or recovery. Repeat both the spiked and unspiked analyses on the diluted aliquot.

a.3.1 If recovery of the analytical spike in the diluted aliquot is greater than or equal to 50%, report the result,

corrected for the dilution.

a.2.2 If analytical spike recovery is again less than 50%, report the result, corrected for the dilution and the recovery of the analytical spike. Flag the data with the following comment:

Recovery of the graphite furnace analytical spike was less than 50%, indicating the presence of a matrix interference. The result, although corrected for the recovery of the analytical spike, is estimated because of the presence of this interference.

b. The original, undiluted sample result is greater than or equal to two times the routine reporting limit:

b.1 If recovery of the analytical spike is 85-115%, report the unspiked sample result. The sample result must fall within the calibration range, although the analytical spike may exceed the high standard provided it recovers within the 85-115% range.

b.2 If recovery of the analytical spike is between 50-85% or between 115-150%, report the unspiked result correcting for the recovery of the analytical spike. Qualify the data with the following comment for that sample:

A single-point, post-digestion spike was performed on this sample analyte. The sample result is corrected for the recovery of the spike on this analyte.

b.3 If recovery of the analytical spike is less than 50% or greater than 150%, dilute the sample by a factor of 2-5, and reanalyze by the method of standard additions as outlined in Section 5.5.

c. The original sample result was over the calibration range and the sample was diluted for reanalysis. The diluted sample result is greater than or equal to two times the routine reporting limit:

c.1 If recovery of the analytical spike is 85-115%, report the unspiked sample result corrected for the dilution.

c.2 If recovery of the analytical spike is not 85-115%, dilute the sample further by a factor of 2-5, if necessary, and reanalyze by the method of standard additions as outlined in Section 5.5.

5.2 SAMPLE PREPARATION CONTROL CHECKS

5.2.1 Preparation Blank (PB) Analysis

A preparation blank, consisting of reagent water processed through sample preparation, is prepared and analyzed with each batch of up to 20 samples digested at the same time.

Evaluate the preparation blank results as follows:

a. If the concentration of the blank is less than or equal to the routine reporting limit, the blank is acceptable.

b. If any analyte concentration in the blank is above the routine reporting limit, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the routine reporting limit, must be redigested and reanalyzed for that analyte. Do not correct the sample concentration for the blank value.

c. If the concentration of the blank is below the negative routine reporting limit, troubleshoot the instrument.

5.2.2 Laboratory Control Sample (LCS) Analysis

A laboratory control sample measures the accuracy of laboratory process. A laboratory control sample is prepared and analyzed for all target analytes for each matrix (water or solid/waste) with each batch of up to 20 samples digested together.

The aqueous LCS spiking solution must be independent (i.e., from a different lot) from the calibration standards.

The solid/waste LCS is a solid reference material. If an analyte of interest is not present in a reference material, spike the analyte into the LCS from a source independent of the calibration standards.

If the percent recovery for an LCS falls outside the control limits, redigest and reanalyze the samples associated with that LCS for the analyte(s) in question. Table 6 lists the current LCS limits for the PE-3030 and 5100. These statistically-based limits are updated semi-annually and subject to change.

Waters analyzed on the PE-4100 have a default control limit of 75 - 125%; solids have the following limits: Sb (42.7 - 467%), Cd (58.4 - 140%), Cr (59.0 - 138%), Pb (53.0 - 140), Ag (40.4 - 146), and Tl (48.4 - 153).

5.2.3 Pre-digestion Spike Sample Analysis

The spike sample analysis provides information about the effect of the sample matrix on the digestion and measurement procedures. Perform at least one spike sample analysis for every batch of 10 samples digested at the same time. Add the spike before digestion, prior to the addition of other reagents.
Calculate individual component percent recoveries (%R) as follows:

$$\%\ Recovery = \frac{(SSR - SR)}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

Note: When the sample concentration is less than the reporting limit, use SR = 0 for purposes of calculating % Recovery.

If the spike recovery is not within the limits of 75-125%, qualify the data for that sample as follows:

This sample was analyzed as a matrix spike. Recovery of the spike was [fill in the recovery] indicating the presence of a matrix interference.

When the sample concentration exceeds the spike concentration by a factor of four or more, flag the spike recovery as follows:

Sample concentration greater than four times spike concentration. Disregard matrix spike recovery value.

5.2.4 Duplicate Sample Analysis

The duplicate sample provides information about the reproducibility of graphite furnace results.

Prepare and analyze one duplicate sample for every 10 samples in a batch digested at the same time.

For results less than five times the reporting limit, and for results in which one falls above five times the reporting limit and one falls below, use a control limit of ±2 x IDL or 20% for waters (±4 x IDL or 40% for soils).

For results greater than five times the reporting limit, calculate the relative percent difference (RPD) as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

where ***RPD*** = Relative Percent Difference
S = First Sample Value (original).
D = Second Sample Value (duplicate)

Limits for precision are listed in Table 6. However, precision limits default to 20% for waters (40% for soils) when the relative error in the reportable sample results exceeds the specified precision limits. Also use these default limits for the PE-4100. The statistically-based limits are updated semi-annually and subject to change.

When precision is unacceptable, reanalyze the duplicate sample. If it remains nonconforming, redigest and reanalyze 25% of the positive results. If reanalysis results do not yield acceptable precision, redigest and reanalyze all samples and report the reanalysis results.

5.3 DETECTION LIMIT DETERMINATION

5.3.1 Instrument Detection Limit (IDL)

Determine instrument detection limits for each instrument used, at least quarterly (every 3 calendar months) for CLP TAL analytes. The IDLs must be less than or equal to the reporting limits.

Determine the Instrument Detection Limits in mg/L as follows:

- Prepare a standard solution of each analyte in reagent water at a concentration 3-5x the manufacturer's suggested IDL initially, then 3-5x the detection limit thereafter.

- Perform seven consecutive measurements of the standard on three nonconsecutive days (thereby obtaining 3 sets of 7 measurements).

  Perform each measurement as if it were a separate analytical sample.

  Calculate the standard deviation (SD) for each set of seven measurements.

- Average the standard deviation values.

- Calculate the IDL (mg/L) by multiplying the average SD by 3.

If the instrument is adjusted in anyway that may affect the IDL, redetermine the IDL.

5.3.2 Method Detection Limit (MDL)

Perform method detection limit studies annually for all analytes. See NUS Laboratory Procedures AP-024, Method Detection Studies.

5.4 DILUTION ANALYSIS

Perform dilution analysis, at client request, to identify matrix interference, as follows:

5.4.1 Withdraw two equal aliquots from the sample. To one of the aliquots, add a known amount of analyte and dilute both aliquots to the same predetermined volume.

- The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4, while keeping in mind that the diluted value should be at least 5 times the instrument detection limit.
- Under no circumstances should the dilution be less than 1:1.

5.4.2 Analyze the diluted aliquots.

5.4.3 Compare the unspiked results, multiplied by the dilution factor, to the original determination.

Agreement of the results within 10% indicates the absence of interference. Comparison of the actual signal from the spike with the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis.

5.5 METHOD OF STANDARD ADDITIONS

When requested or as indicated in Section 5.1.6 above, the method of standard additions (MSA) is used to compensate for matrix effects. MSA involves the analysis of an unspiked aliquot of sample and three additional aliquots spiked at varying levels. The unspiked sample result must be at least 5 times the reporting limit, whenever possible. All of the spiked aliquots must be within the linear range.

The method of standard additions is performed as follows:

5.5.1 Keep dilutions at a minimum. Larger or successive dilutions may be required if severe matrix interference is encountered (i.e., very low or no spike recovery).

5.5.2 Begin MSA by preparing and analyzing one unspiked (0 ADD) aliquot.

5.5.3 Based on the 0 ADD result, determine the appropriate spiking levels:

a. **0 ADD result ≥ 10 x RL:** Prepare three additional spikes at approximately 50%, 100% and 150% of the concentration of the unspiked (0 ADD) aliquot. Maintain the volume of sample and final volume in the 0 ADD aliquot throughout all spikes.

Calculate the x-intercept, slope, and correlation coefficient of the best fit line using a calculator having these statistical capabilities. If the correlation coefficient of the MSA is greater than or equal to 0.995, calculate the final result by multiplying the absolute value of the x-intercept by the dilution factor. If the correlation coefficient is less than 0.995, repeat the MSA once, employing additional dilution if deemed necessary. If the correlation coefficient on the second MSA is again less than 0.995, calculate a result from the MSA with the better correlation, and flag the data as follows:

Result was obtained by the method of standard addition, A linear correlation could not be established. Matrix interference is suspected.

b. **RL ≤ 0 ADD result < 10 x RL:** Prepare three additional spikes at 5, 10 and 15 times the detection limit, whenever linear range permits. Maintain the volume of sample and final volume in the 0 ADD aliquot throughout all spikes.

Calculate the x-intercept, slope, and correlation coefficient of the best fit line using a calculator having these statistical capabilities. If the correlation coefficient of the MSA is greater than or equal to 0.995, calculate the final result by multiplying the absolute value of the x-intercept by the dilution factor. If the correlation coefficient is less than 0.995, repeat the MSA once. If the correlation coefficient on the second MSA is again less than 0.995, calculate a result from the MSA with the better correlation, and flag the data with the note described in step a, above.

c. **0 ADD result < RL:** Prepare two additional spikes at 5 and 10 times the detection limit, whenever linear range permits. Maintain the volume of sample and final volume in the 0 ADD aliquot throughout all spikes.

If recovery of either spike is <40%, prepare the 0 ADD aliquot and two additional spikes, employing an additional 5 or 10 fold dilution. If recovery is still <40%, report the result of the largest dilution. Flag the data with the following:

Result was obtained by the method of standard addition. Although the reported result is below the detection limit, spike recovery was less than 40% - matrix interference is suspected.

6.0 INTERFERENCES

6.1 Soil/sediment/sludge samples are diverse and complex matrices. Both the LCS and the matrix spike samples are analyzed to evaluate the acid digestion procedure's effectiveness for a given waste type.

6.2 Glassware must be scrupulously clean to prevent cross contamination at trace

levels. Griffin beakers should be replaced periodically as they tend to etch and hold traces of contamination.

6.3 Though the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered.

To verify the absence of matrix or chemical interference, post-digestion spiking is used. Treat samples that indicate the presence of interference in one or more of the following ways:

- Analyze the sample by the method of standard additions.
- Successively dilute and analyze the samples to eliminate interferences.
- Modify the sample matrix either to remove interferences or to stabilize the analyte. Addition of ammonium nitrate removes alkali chlorides; addition of ammonium phosphate retains cadmium. Mixing hydrogen with the inert purge gas aids in molecular dissociation through chemical reduction.

6.4 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. Zeeman background correction is employed. Background correction may also compensate for nonspecific broad-band absorption interference.

6.5 Interference from a smoke-producing sample matrix can be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Use care to prevent loss of the analyte.

6.6 Oxidize samples containing large amounts of organic materials by conventional acid digestion before analyzing in the furnace to minimize broad-bank absorption.

6.7 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. Minimize the amount of other acids used in addition to nitric, particularly hydrochloric and, to a lesser extent, sulfuric and phosphoric acids. The exception here is Sb and Sn analyses, which require digestion and dilution with hydrochloric acid.

6.8 Carbide formation resulting from the chemical environment of the furnace has been observed. Reduce carbide formation and increase sensitivity with the use of pyrolytically coated graphite tubes.

6.9 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will

then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal.

Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. Reduce this type of interference by narrowing the slit width.

6.10 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The following precautions are necessary to reduce contamination interference:

- Keep the sample preparation work area scrupulously clean.
- Clean all glassware as directed in the glassware cleaning procedure, AP-018.
- Soak pipet tips suspected of contamination with 1:5 HNO_3 and rinse thoroughly with tap and reagent water.

  Note: Pipet tips are a frequent source of contamination. The use of a better grade of pipet tip can greatly reduce this problem.

- Give close attention to reagent blank results.
- Clean the pyrolytic graphite tube before use with five to ten high-temperature burns.

6.11 Memory effects occur when the analyte is not totally volatized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. Clean the tube by operating the furnace at full power for the required time period, as needed, at regular intervals during analysis.

7.0 SAFETY PRECAUTIONS

7.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

7.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.2 Handle and store all reagents in accordance with the precautions listed on the Material Safety Data Sheets (MSDS).

7.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.4 Handle all glass equipment with care.

7.5 When preparing dilute solutions of concentrated acids, ALWAYS ADD ACID to WATER.

7.6 Perform all acid digestions under an operating fume hood.

8.0 APPARATUS AND MATERIALS

8.1 Griffin beakers: 150-mL capacity, or equivalent glassware.

Note: Beakers will tend to etch over time and should be replaced periodically.

8.2 Watch glasses: ribbed and plain, or similar covers.

8.3 Pipets: Volumetric class A, assorted sizes.

8.4 Filter paper: Whatman #41.

8.5 Filter funnels.

8.6 Graduated cylinders: 100-mL capacity. Verify that the volumetric accuracy is within 2% upon receipt of new graduates.

8.7 Volumetric flasks: 100-mL, class A.

8.8 Hot plate: Thermolyne, Lindberg, or equivalent.

8.9 Atomic absorption spectrometer: Perkin-Elmer 3030, Perkin-Elmer 5100, Perkin-Elmer 4100, or equivalent.

8.10 Graphite furnace: Perkin-Elmer HGA-600,or equivalent.

8.11 Graphite furnace tubes: CPI, PE, or equivalent.

8.12 Contact cylinders: PE, for Zeeman furnaces (3030/5100); PE THGA (4100)

8.13 Autosampler: Perkin-Elmer AS-60, Perkin-Elmer AS-70, or equivalent.

8.14 Electrodeless discharge lamps (EDL): Single element lamps used for As, Se, and Pb analyses.

8.15 Hollow cathode lamps (HC): Single element lamps.

8.16 Mircoliter pipets: With disposable tips. Sizes can range from 5 to 1000 μL as required.

Note: Pipet tips should be checked as a possible source of contamination prior to their use.

8.17 Pressure-reducing valves: Maintain the argon supply at a pressure somewhat higher than the controlled operating pressure of the instrument by suitable valves.

8.18 Conical sample cups: Clear polystyrene, unsterile.

8.19 Recirculator: Brinkmann RM 20 Lauda

8.20 Cotton Swabs.

9.0 REAGENTS

9.1 Reagent water: Deionized water passed through a mixed bed resin column. Use reagent water for the preparation of all reagents and calibration standards and as dilution water.

9.2 Nitric acid (HNO_3, 1:1): Trace metals grade acid certified for AA use. Prepare a 1:1 dilution with reagent water by adding the concentrated acid to an equal volume of water.

9.3 Hydrochloric acid (HCl, 1:1): Trace metals grade acid certified for AA use. Prepare a 1:1 dilution with reagent water by adding the concentrated acid to an equal volume of water.

9.4 Hydrogen peroxide (H_2O_2, 30%): ACS grade, 30% solution.

9.5 Argon gas: Prepurified grade.

9.6 Stock standards for each analyte metal: purchased commercially. Standards must be suitable for GFAA analysis and traceable to NIST standards.

Matrix spikes and laboratory control samples, as identified in Section 5.0, are prepared by spiking 0.50 mL of the following solutions, as necessary for the appropriate analytes, into 100-mL sample or reagent water aliquots.

9.6.1 **GFAA Spiking Cocktails:** purchased premade from High Purity, or equivalent. All cocktails are 5% HNO_3 by volume. See Table 1 for concentrations.

a. GFAA A: Al, Be, Cd, Cr, Cu, Fe, Mn, Mo, Pb, Tl, V

b. GFAA B: Sn

9.6.2 **GFAA Silver Standard:** a 10 ppm working standard for silver is prepared by diluting 2.0 mL of a 1000 ppm stock silver standard to 200 mL in a volumetric flask with 2% HNO_3. The working standard is transferred to a clean, brown glass bottle, labeled and dated. This working standard expires in 1 month.

Note: Pipettes are NOT to be inserted into either the stock silver standard or the working standard. To obtain aliquots, pour small amounts of the standard into separate disposable cups and pipet aliquots from these cups. Discard any excess standard remaining in the disposable cups. DO NOT RETURN EXCESS to original standard container.

9.7 Calibration and detection limit standards: See Table 4 for standards concentrations.

Standard solutions are acidified as follows:

- As/Se in 1% HNO_3 and 2% H_2O_2.
- Sb in 5% HNO_3 and 2.5% HCl for soils.
  Sb in 1% HNO_3 and 5% HCl for waters.
- All other analytes in 1% HNO_3.

9.8 Calibration blank/dilution water: Reagent water acidified to specifications listed in Section 10.7, above.

9.9 Isopropyl alcohol: Reagent grade.

9.10 Matrix Modifiers: Purchase stock chemicals commercially; Cadmium modifier must be purchased from Fluka.

Use 100 µL of the appropriate modifier to 1000 µL of sample.

9.10.1 **Arsenic/Selenium Modifier -- Nickel Nitrate:**

Prepare working solution by dissolving 24.78 g nickel nitrate in approximately 300 mL reagent water using a 500-mL volumetric flask. Dilute to volume with reagent water.

9.10.2 **Chromium Modifier -- Calcium Nitrate:**

Prepare stock solution by dissolving 11.8 g calcium nitrate in approximately 70 mL reagent water using a 100-mL volumetric flask. Dilute to volume with reagent water. Prepare working solution by making a 10x dilution of the stock solution using reagent water.

9.10.3 **Cadmium Modifier -- Diammonium Hydrogen Phosphate:**

Prepare working solution by dissolving 8.0 g of diammonium hydrogen phosphate in approximately 70 mL reagent water using a 100-mL volumetric flask. Dilute to volume with reagent water.

9.10.4 **Lead Modifier -- Lanthium Nitrate:**

Prepare working solution by dissolving 5.8 g of lanthium oxide in 10.0 mL of HNO_3 using a 100 mL volumetric flask. Dilute to volume with reagent water.

10.0 REFERENCES

10.1 U.S. EPA. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, revised March,1983. 200-series Methods.

10.2 U.S. EPA. "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods," SW-846, 1986. 7000-series Methods.

10.3 American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989. Method 3113-B.

TABLE 1
GRAPHITE FURNACE ATOMIC ABSORPTION REPORTING LIMITS

Metal	Reporting Limit (mg/L)	(mg/kg)
Aluminum	0.003	0.3
Antimony	0.01	1
Antimony (residential well analysis)	0.005*	--
Arsenic	0.003	0.3
Arsenic (residential well analysis)	0.002	--
Beryllium	0.0005	0.05
Cadmium	0.0005	0.05
Chromium	0.001	0.1
Copper	0.002	0.2
Iron	0.002	0.2
Lead	0.002	0.2
Molybdenum	0.002	0.2
Selenium	0.004	0.4
Silver	0.0005	0.05
Thallium	0.002	0.2
Tin	0.005	0.05
Vanadium	0.004	0.4

* This limit involves a double injection of sample (PE-5100 only).

TABLE 2A
GFAA PERKIN-ELMER 3030 OPERATING CONDITIONS

Element	User Program Name/#	Wavelength (nm)	Slit (nm)	Lamp Type/ Current[1]	Time (sec)		Graphite Tube Type[2]	Autosampler Volume (µL)	Rollover Absorbance
					Integ.	Display			
Aluminum	AL	309.3	0.7	HC/25	3	3	PG	20	1.000
Antimony	SB	217.6	0.2	HC/20	5	5	PG	10	3.000
Arsenic	AS	193.7	0.7	EDL/8	5	5	PG	30	1.000
Beryllium	BE	234.9	0.7	HC/30	5	5	PG	20	1.00
Cadmium	CD	228.8	0.7	HC/4	7	7	PG	10	1.00
Chromium	CR	357.9	0.7	HC/25	4	5	PG	15	1.30
Copper	CU	324.7	0.7	HC/15	4	4	PG	20	1.00
Iron	FE	248.3	0.2	HC/30	4	6	PG	20	1.00
Lead	PB	283.3	0.7	EDL/10	4	5	PG	20	1.00
Molybdenum	MO	313.3	0.7	HC/30	12	4	PU	10	2.00
Selenium	SE	196.0	0.7	EDL/6	4	4	PG	30	1.00
Silver	AG	328.1	0.7	HC/10	5	5	PG	20	1.00
Thallium	TL	276.8	0.7	HC/20	5	4	PG	25	1.50
Vanadium	V	318.4	0.7	HC/30	5	5	PU	15	1.00

[1] Lamp type - HC = Hollow cathode; EDL = Electrodeless Discharge Lamp

[2] Graphite tube type - PG = Pyrocoated, groved; PU = Pyrocoated, ungrooved; NPG = Non-pyrocoated, grooved; NPU = Non-pyrocoated, ungrooved

NOTE: The following operating conditions apply to all of the above elements:

Gas type - Argon, 53 psi at regulator
Signal Processing - Peak Area
Analysis Mode - Zeeman
Furnace Cooling Method - Tap water or Recirculator, if available
Replicates - 2
Screen Format - Basic data; Supplimental data (calibration only)
Statistics - Average, standard deviation, and coefficient of variation
Blank, Standard, Sample Units - mg/L
Print - Main values; Main values and supplemental data (calibration only)

TABLE 2B
GFAA PERKIN-ELMER 5100 OPERATING CONDITIONS

Element	User Program Name/#	Wavelength (nm)	Slit (nm)	Lamp Type/ Current[1]	Time (sec)		Graphite Tube Type[2]	Autosampler Volume (µL)	Rollover Absorbance
					Integ.	Display			
Aluminum	ALDL	309.3	0.7	HC/25	5	5	PG	20	1.00
Antimony	SBDL	217.6	0.2	HC/20	5	5	PG	10	3.000
Arsenic	ASDL	193.7	0.7	EDL/6	5	5	PG	30	1.00
Beryllium	BEDL	234.9	0.7	HC/30	5	5	PG	15	1.00
Cadmium	CDDL	228.8	0.7	HC/4	5	5	PG	10	1.00
Chromium	CRDL	357.9	0.7	HC/25	4	5	PG	20	1.30
Copper	CUDL	324.7	0.7	HC/15	5	5	PG	15	1.00
Iron	FEDL	248.3	0.2	HC/30	5	5	PG	20	1.00
Lead	PBDL	283.3	0.7	EDL/7.5	4	5	PG	20	1.40
Selenium	SEDL	196.0	2.00	EDL/4	7	7	PG	30	1.40
Silver	AGDL	328.1	0.7	HC/10	5	7	PG	20	1.00
Thallium	TLDL	276.8	0.7	HC/20	5	7	PG	20	1.50
Tin	SNDL	286.3	0.7	HC/30	5	—	NPU	40	1.50

[1] Lamp type - HC = Hollow cathode; EDL = Electrodeless Discharge Lamp

[2] Graphite tube type - PG = Pyrocoated, groved; PU = Pyrocoated, ungrooved; NPG = Non-pyrocoated, grooved; NPU = Non-pyrocoated, ungrooved

NOTE: The following operating conditions apply to all of the above elements:

Gas type - Argon, 53 psi at regulator
Signal Processing - Peak Area
Analysis Mode - Zeeman
Furnace Cooling Method - Tap water
Replicates - 2
Screen Format - Basic data; Supplimental data (calibration only)
Statistics - Average, standard deviation, and coefficient of variation
Blank, Standard, Sample Units - mg/L
Print - Main values; Main values and supplemental data (calibration only)
Save All Data - Yes

TABLE 2C
GFAA PERKIN-ELMER 4100 OPERATING CONDITIONS

Element	User Program Name/#	Wavelength (nm)	Slit (nm)	Lamp Type/ Current[1]	Time (sec)		Graphite Tube Type[2]	Autosampler Volume (µL)	Rollover Absorbance
					Integ.	Display			
Antimony	SBDL	217.6	0.2	HC/20	5	5	PG	20	2.0
Cadmium	CDDL	228.8	0.7	HC/4	5	5	PG	10	1.00
Chromium	CRDL	357.9	0.7	HC/25	4	5	PG	20	1.30
Lead	PBDL	283.3	0.7	HC/10	4	5	PG	20	1.40
Silver	AGDL	328.1	0.7	HC/10	5	7	PG	20	1.00
Thallium	TLDL	276.8	0.7	HC/20	5	7	PG	20	1.50

[1] Lamp type - HC = Hollow cathode; EDL = Electrodeless Discharge Lamp

[2] Graphite tube type - PG = Pyrocoated, groved; PU = Pyrocoated, ungrooved; NPG = Non-pyrocoated, grooved; NPU = Non-pyrocoated, ungrooved

NOTE: The following operating conditions apply to all of the above elements:

Gas type - Argon, 53 psi at regulator
Signal Processing - Peak Area
Analysis Mode - Zeeman
Furnace Cooling Method - Tap water or Recirculator, if available
Replicates - 2
Screen Format - Basic data; Supplimental data (calibration only)
Statistics - Average, standard deviation, and coefficient of variation
Blank, Standard, Sample Units - mg/L
Print - Main values; Main values and supplemental data (calibration only)

TABLE 3A
GFAA PERKIN-ELMER 3030 TEMPERATURE PROGRAM[1]

Element	Step	Furnace Temperature (°C)	Time (sec)		Internal Gas Flow	Gas Type (N or A)	Read
			Ramp	Hold			
Aluminum	1	200	30	20	300	A	
	2	1100	10	20	300	A	
	3	20	1	1	300	A	
	4	2500	0	3	0	A	*
	5	2700	1	2	300	A	
	6	20	1	1	300	A	
Antimony	1	170	10	30	300	A	
	2	1100	5	20	300	A	
	3	20	1	5	300	A	
	4	2500	0	5	20	A	*
	5	2700	1	5	300	A	
Arsenic	1	150	10	30	300	A	
	2	1100	10	20	300	A	
	3	20	1	5	300	A	
	4	2400	0	5	0	A	*
	5	2500	2	3	300	A	
Beryllium	1	150	25	25	300	A	
	2	900	30	30	300	A	
	3	20	1	5	300	A	
	4	2500	0	4	0	A	
	5	2600	1	5	300	A	
Cadmium	1	160	5	30	300	A	
	2	700	5	20	300	A	
	3	20	1	5	300	A	
	4	1600	0	7	50	A	*
	5	2400	1	3	300	A	
Chromium	1	150	5	30	300	A	
	2	1000	5	30	300	A	
	3	20	1	5	300	A	
	4	2500	0	4	100	A	*
	5	2700	2	3	300	A	
Copper	1	150	10	20	300	A	
	2	1000	10	20	300	A	
	3	20	1	5	300	A	
	4	2500	0	4	0	A	*
	5	2600	2	4	300	A	

TABLE 3A (CONT'D)
GFAA PERKIN-ELMER 3030 TEMPERATURE PROGRAM[1]

Element	Step	Furnace Temperature (°C)	Time (sec)		Internal Gas Flow	Gas Type (N or A)	Read
			Ramp	Hold			
Iron	1	80	2	0	300	A	
	2	250	30	30	300	A	
	3	1000	30	30	300	A	
	4	20	1	5	300	A	
	5	2400	0	4	20	A	*
	6	2700	2	3	300	A	
	7	20	2	10	300	A	
Lead	1	170	10	30	300	A	
	2	900	5	30	300	A	
	3	20	1	5	300	A	
	4	1800	0	4	0	A	*
	5	2400	2	3	300	A	
Molybdenum	1	150	20	20	300	A	
	2	1100	10	20	300	A	
	3	20	1	5	300	A	
	4	2700	0	12	0	A	*
	5	2800	2	5	300	A	
	6	20	1	5	300	A	
	7	2800	2	5	300	A	
Selenium	1	150	10	40	300	A	
	2	1100	10	20	300	A	
	3	20	1	5	300	A	
	4	2200	0	4	0	A	*
	5	2500	2	3	300	A	
Silver	1	200	10	30	300	A	
	2	700	10	30	300	A	
	3	20	1	5	300	A	
	4	2100	0	5	0	A	*
	5	2500	1	2	300	A	
Thallium	1	170	10	30	300	A	
	2	300	5	10	300	A	
	3	20	1	5	300	A	
	4	1400	0	5	0	A	*
	5	2500	2	3	300	A	
Vanadium	1	150	20	20	300	A	
	2	1100	10	20	300	A	
	3	20	2	5	300	A	
	4	2700	0	5	0	A	*
	5	2700	1	5	300	A	

[1] Temperature program may require minute, daily modifications depending upon room temperature, atmospheric conditions, etc.

TABLE 3B
GFAA PERKIN-ELMER 5100 TEMPERATURE PROGRAM[1]

Element	Step	Furnace Temperature (°C)	Time (sec)		Internal Gas Flow	Gas Type (N or A)	Read
			Ramp	Hold			
Aluminum	1	150	10	40	300	A	
	2	1100	10	30	300	A	
	3	20	1	5	300	A	
	4	2500	0	5	0	A	*
	5	2600	1	5	300	A	
Antimony	1	170	5	40	300	A	
	2	900	1	30	300	A	
	3	20	1	5	300	A	
	4	2500	0	5	20	A	*
	5	2600	1	5	300	A	
Arsenic	1	170	20	30	300	A	
	2	600	10	30	300	A	
	3	20	1	5	300	A	
	4	2300	0	5	0	A	*
	5	2500	1	5	300	A	
Beryllium	1	170	10	30	300	A	
	2	900	15	30	300	A	
	3	20	1	5	300	A	
	4	2650	0	5	40	A	*
	5	2650	1	5	300	A	
Cadmium	1	170	5	30	300	A	
	2	500	5	30	300	A	
	3	20	1	5	300	A	
	4	1600	0	5	30	A	*
	5	2600	1	2	300	A	
Chromium	1	170	10	30	300	A	
	2	900	15	25	300	A	
	3	20	1	5	300	A	
	4	2650	0	4	80	A	*
	5	2600	2	3	300	A	
Copper	1	170	10	30	300	A	
	2	800	1	30	300	A	
	3	20	1	5	300	A	
	4	2500	0	5	0	A	*
	5	2600	1	5	300	A	

TABLE 3B (CONT'D)
GFAA PERKIN-ELMER 5100 TEMPERATURE PROGRAM[1]

Element	Step	Furnace Temperature (°C)	Time (sec)		Internal Gas Flow	Gas Type (N or A)	Read
			Ramp	Hold			
Iron	1	120	1	50	300	A	
	2	1400	1	30	300	A	
	3	20	1	15	300	A	
	4	2400	0	5	20	A	*
	5	2600	1	5	300	A	
Lead	1	150	10	40	300	A	
	2	900	5	30	300	A	
	3	20	1	5	300	A	
	4	1600	0	4	0	A	*
	5	2500	1	3	300	A	
Selenium	1	170	10	30	300	A	
	2	600	5	20	300	A	
	3	20	1	5	300	A	
	4	2100	0	7	0	A	*
	5	2800	1	5	300	A	
Silver	1	170	1	30	300	A	
	2	800	1	30	300	A	
	3	20	1	5	300	A	
	4	2100	0	5	0	A	*
	5	2600	1	5	300	A	
Thallium	1	150	10	30	300	A	
	2	300	5	10	300	A	
	3	20	1	3	300	A	
	4	1400	0	5	0	A	*
	5	2500	1	4	300	A	
Tin	1	150	10	40	300	A	
	2	1100	15	15	300	A	
	3	20	1	15	300	A	
	4	2500	0	5	0	A	*
	5	2500	1	5	300	A	
	6	20	1	5	300	A	

[1] Temperature program may require minute, daily modifications depending upon room temperature, atmospheric conditions, etc.

TABLE 3C
GFAA PERKIN-ELMER 4100 TEMPERATURE PROGRAM[1]

Element	Step	Furnace Temperature (°C)	Time (sec)		Internal Gas Flow	Gas Type (N or A)	Read
			Ramp	Hold			
Antimony	1	120	1	30	250	A	
	2	150	10	30	250	A	
	3	1400	10	20	250	A	
	4	1900	0	8	0	A	•
	5	2400	1	2	250	A	
Cadmium	1	120	1	20	250	A	
	2	140	10	30	250	A	
	3	200	5	10	250	A	
	4	500	10	20	250	A	•
	5	1200	0	5	0	A	
	6	2400	1	2	250	A	
Chromium	1	120	1	20	250	A	
	2	140	120	30	250	A	
	3	200	5	10	250	A	
	4	1100	10	20	250	A	•
	5	2100	0	4	0	A	
	6	2400	1	2	250	A	
Lead	1	120	1	30	250	A	
	2	150	10	30	250	A	
	3	200	5	10	250	A	
	4	600	10	20	250	A	•
	5	1400	0	3	300	A	
	6	2400	1	2	250	A	
Silver	1	120	1	20	250	A	
	2	150	5	30	250	A	
	3	600	10	20	250	A	
	4	1200	0	5	0	A	•
	5	2400	1	2	250	A	
Thallium	1	120	1	30	250	A	
	2	150	10	30	250	A	
	3	200	10	20	250	A	
	4	1600	0	5	0	A	•
	5	2400	1	2	250	A	

[1] Temperature program may require minute, daily modifications depending upon room temperature, atmospheric conditions, etc.

TABLE 4
GFAA PERKIN-ELMER 3030, 5100, AND 4100 CALIBRATION CONDITIONS

Element	Standard Conc. (mg/L)	Matrix Modifier/Preparation	Sample Preparation	Calibration Type
Aluminum	0.01, 0.025, 0.04	------	------	Nonlinear
Antimony	0.06, 0.12, 0.20	------	------	Nonlinear
Arsenic	0.01, 0.025, 0.04	$Ni(NO_3)_2$ Weigh 24.78 g $Ni(NO_3)_2$ and dilute to 500 mL with deionized H_2O	1000 µL blank, standard, sample plus 100 µL matrix modifier	Nonlinear
Beryllium	0.001, 0.0025, 0.004	------	------	Nonlinear
Cadmium	0.0025, 0.005, 0.0075	$(NH_4)_2HPO_4$ Weigh 8 g $(NH_4)_2HPO_4$ stock and dilute to 100 mL with deionized H_2O	1000 µL blank, standard, sample plus 100 µL matrix modifier	Nonlinear
Chromium	0.01, 0.025, 0.04	$Ca_2(NO_3)\cdot 4H_2O$ Weigh 11.8 g $Ca_2(NO_3)_2\cdot 4H_2O$ and dilute to 100 mL with deionized H_2O. Aliquot 5 mL stock + 5 mL H_2O_2 per 50 mL for working solution	1000 µL blank, standard, sample plus 100 µL matrix modifier	Nonlinear
Copper	0.01, 0.025, 0.04	------	------	Nonlinear
Iron	0.01, 0.025, 0.04	------	------	Nonlinear
Lead	0.01, 0.025, 0.04	$La_2(NO_3)_2$ Dilute 5.8 g La_2O_3 and 10 mL HNO_3 to 100 mL with deionized H_2O	1000 µL blank, standard, sample plus 100 µL matrix modifier	Nonlinear
Molybdenum[1]	0.025, 0.050, 0.075	------	------	Nonlinear
Selenium	0.01, 0.025, 0.04	$Ni(NO_3)_2$ Weigh 24.78 g $Ni(NO_3)_2$ and dilute to 500 mL with deionized H_2O	1000 µL blank, standard, sample plus 100 µL matrix modifier	Nonlinear
Silver	0.005, 0.0075, 0.01 (PE 3030)	------	------	Nonlinear
Thallium	0.01, 0.02, 0.03 (PE 3030 & 5100)	------	------	Nonlinear
	0.01, 0.025, 0.05 (PE 4100)	------	------	Nonlinear
Tin[2]	0.1, 0.15, 0.20	------	------	Nonlinear
Vanadium[1]	0.010, 0.025, 0.040	------	------	Nonlinear

[1] PE 3030 model only.
[2] PE 5100 model only.

TABLE 5
GFAA ANALYSIS SEQUENCE

	Run #	Sample	Key
Instrument warmup and stabilization			
Initial calibration:	1	CB	CB = calibration blank
	2	S1	S1 = low conc. calibration standard
	3	S2	S2 = middle conc. calibration standard
	4	S3	S3 = high conc. calibration standard
Initial QC checks:	5	ICV	ICV = initial calibration verification
	6	ICB	ICB = initial calibration blank
	7	RLS	RLS = reporting limit standard
Sample analysis:	8	SX	SX = digestate; includes field samples, duplicates, matrix spikes, prep blanks, lab control standards. All field samples, except those analyzed as duplicate/matrix spike, must be single-spiked.
	9	SX	
	10	SX	
	11	SX	
	12	SX	
	13	SX	
	14	SX	
	15	SX	
	16	SX	
	17	SX	
Continuing QC checks:	18	CCS	CCS = continuing calibration standard
	19	CCB	CCB = continuing calibration blank
Repeat sample analysis and continuing calibration cycle until all samples are analyzed.			
Final QC checks:	n-1	CCS	n = last sequence number in run
	n	CCB	

TABLE 6
LABORATORY CONTROL SAMPLES (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
WATER MATRICES - INSTRUMENT 3030
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery [2]	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L01W, Antimony	AC22	Range: --- RPD: ---	Range: ≤2X IDL RPD: ≤20%	--- ---	--- ---	--- ---	78.8-113	70.2-122	95.98	8.60	0.43	77.7-113	68.9-122	95.41	8.84
L40, Arsenic	CA01	Range: --- RPD: ≤14.1%	Range: ≤2X IDL RPD: ≤19.2%	--- 4.12	--- 5.01	--- 0.39	84.8-105	79.8-110	94.79	5.00	0.65	60.9-110	48.6-122	85.33	12.33
L02W, Cadmium	AC13	Range: --- RPD: ---	Range: ≤2X IDL RPD: ≤20%	--- ---	--- ---	--- ---	90.6-115	84.6-121	102.73	6.05	0.68	77.6-133	63.9-146	105.08	13.72
L02W, Lead	AB35	Range: --- RPD: ≤14.1%	Range: ≤2X IDL RPD: ≤18.9%	--- 4.56	--- 4.79	--- 0.38	80.4-113	72.3-121	96.49	8.06	0.48	30.6-112	10.2-133	71.34	20.39
L40, Selenium	CA03	Range: --- RPD: ---	Range: ≤2X IDL RPD: ≤20%	--- ---	--- ---	--- ---	77.4-111	68.8-120	94.43	8.53	0.37	41.4-116	22.6-135	78.87	18.76

PM = preparation method
x = mean
s = standard deviation
LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit
NA = not applicable

[1] Cpk based on 10% RPD specification goal.
[2] Cpk based on 85-115% recovery specification goal.

TABLE 6 (CONT'D)
LABORATORY CONTROL SAMPLES (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
SOLID MATRICES - INSTRUMENT 3030
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L04S, Arsenic	BA43	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--- ---	--- ---	--- ---	69.2-117	48.5-153	92.97	11.86	0.51	12.2-171	0-211	91.73	39.78
L04S, Lead	BA47	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--- ---	--- ---	--- ---	66.6-118	53.0-140	92.29	12.87	0.45	0-184	0-230	91.82	46.11
L04S, Selenium	BA49	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--- ---	--- ---	--- ---	65.3-132	48.5-146	98.82	16.74	0.47	20.6-111	0-133	65.72	22.56

PM = preparation method
x = mean
s = standard deviation
LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit
[1] Cpk based on 20% RPD specification goal.
[2] Cpk based on 75-125% recovery specification goal.

TABLE 6 (CONT'D)
LABORATORY CONTROL SAMPLES (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
WATER MATRICES - INSTRUMENT 5100
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L01W, Antimony	AC25	Range: --- RPD: ---	Range: ≤2X IDL RPD: ≤20%	--- ---	--- ---	--- ---	75.7-117	65.2-128	96.57	10.44	0.37	79.8-116	70.8-125	97.79	8.99
L40, Arsenic	CA02	Range: --- RPD: ≤14.3%	Range: ≤2X IDL RPD: ≤19.1%	--- 4.86	--- 4.74	--- 0.36	89.1-107	84.6-112	98.21	4.55	0.97	57.2-113	43.4-126	84.88	13.82
L02W, Cadmium	AC14	Range: --- RPD: ---	Range: ≤2X IDL RPD: ≤20%	--- ---	--- ---	--- ---	88.0-121	79.9-129	104.28	8.13	0.44	83.2-135	70.4-147	108.89	12.84
L02W, Lead	AB24	Range: --- RPD: ≤13.8%	Range: ≤2X IDL RPD: ≤18.4%	--- 4.71	--- 4.55	--- 0.39	85.7-115	78.5-122	100.17	7.22	0.68	33.0-124	10.3-147	78.53	22.74
L40, Selenium	CA04	Range: --- RPD: ≤10.2%	Range: ≤2X IDL RPD: ≤13.3%	--- 3.82	--- 3.17	--- 0.65	84.8-113	77.7-120	98.92	7.07	0.66	53.2-116	37.6-131	84.50	15.64

PM = preparation method
x = mean
s = standard deviation
[1] Cpk based on 10% RPD specification goal.

LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit
[2] Cpk based on 85-115% recovery specification goal.

TABLE 6 (CONT'D)
LABORATORY CONTROL SAMPLES (LCS) CONTROL LIMITS

QUALITY CONTROL TEST FILE - METALS
SOLID MATRICES - INSTRUMENT 5100
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x	s	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	x	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x	s
L04S, Arsenic	BA44	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--------- ---------	------ ------	------ ------	69.4-122	48.5-153	95.89	13.23	0.53	2.0-183	0-229	92.64	45.32
L04S, Lead	BA48	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--------- ---------	------ ------	------ ------	76.6-131	53.0-140	103.85	13.66	0.52	--------	--------	--------	--------
L04S, Selenium	BA50	Range: --- RPD: ---	Range: ≤4X IDL RPD: ≤40%	--------- ---------	------ ------	------ ------	69.5-135	48.5-146	102.06	16.27	0.47	22.3-135	0-164	78.87	28.29

PM = preparation method
x = mean
s = standard deviation
LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit
[1] Cpk based on 20% RPD specification goal.
[2] Cpk based on 75-125% recovery specification goal.

FIGURE 1
LOGBOOK PAGE

Cr by GFAA start time 2119 Routine P381-92 121

Element Chromium Instrument PE5100
Wavelength 357.9 nm Standard Reference P244552-201
Matrix Modifier Pd(NO3)2 3-DMA-91-203 Background Correction D2
Modifier Reference ___ Integration Time 4 secs
Sample Aliquot 20 µL Lamp/Serial No PHL76721
Characteristic Mass: Calibration Verification:
Standard ___ Source Accu CRM #4645
Absorbance ___ True Value 100.3
C.M. Value ___ Prep. Date 8-10-92-203
Percent True Value ___

Run File 30106CR1

HGA TEMPERATURE PROGRAM

STEP NO.	TEMP. (°C)	RAMP (SEC)	HOLD (SEC)	STEP I.D.
1	170	10	30	
2	900	15	25	
3	20	1	5	
4	2650	0	4	min Flow Read (80)
5	2600	2	3	

Analytical spike prepared by adding 100ul of a 5ppb 0.2mg/L Solution to 100ml of sample. All Standards and unspiked samples contain 100ul of 4% HNO3 solution

Seq #	Sample ID	M.I	Spike	comment
1	Blank			
2	001			
3	0.025			
4	0.04			
5	FCV	Start Flow		
6	FCB			
7	RICO001			
8	222506			PB Batch 15502
9	222505			LCS
10	221165			
11	221165A		0.02	
12	221166			
13	221166A		0.02	
14	Dup			
15	MS			
16	CCV1			
17	CCB1			

Philip Smith 09640 1/6/92
Cl mott 1/8/93

FIGURE 2
PRINTED WORKSHEET

WORKSHEET
January 06, 1993
Flame/Graphite Furnace

Analyte: Chromium, Dissolved, Low Level (Cr) BATCH 15502

Sample	Type	Client	Date Sampled	Date Received	Date Due	Prep	Anls	Sample Description
221165	ORIG		16-DEC-92	18-DEC-92	05-JAN-92	L06WFEZ-	ACR02E-	OLD ASHFILL CELL
221166	DUP		16-DEC-92	18-DEC-92	05-JAN-92	L06WFEZ-	ACR02E-	NEW ASHFILL CELL
221166	MS		16-DEC-92	18-DEC-92	05-JAN-92	L06WFEZ-	ACR02E-	NEW ASHFILL CELL
221166	ORIG		16-DEC-92	18-DEC-92	05-JAN-92	L06WFEZ-	ACR02E-	NEW ASHFILL CELL
222505	LCSR	HALLIBURTON NUS ENVIRONME	06-JAN-93	06-JAN-93		L06W	ACR02E-	Lab Control Sample
222506	BLNK	HALLIBURTON NUS ENVIRONME	06-JAN-93	06-JAN-93		L06W	ACR02E-	Method Blank

SAMPLE INSTRUCTIONS

* * * * * * * * * * * *

Ref.	Analysis Date	Instrument	Anlst	Start Time	Run File	Comments
1	1/6/93	PE5100	0960	2119	30106CR1	
2						
3						
4						
5						

Sample	Type	Ref	Diln.	Cup	Result	Unit	Book	Page	Range	RPD	MSR % Rec	TV/SA	Reviewed
221165	ORIG			10	0.006	mg/l	PJ81-92	121					CA
221166	ORIG			12	0.356								
221166	DUP			3	0.0349				0.321				
221166	MS			5	0.0216						77.5	0.02	
222505	LCSR			9	0.0203						102	0.32	
222506	BLNK			4	<0.001								

FIGURE 3
COMPUTER PRINTOUT

```
-------------------------------------------------------------------------------
ID: ICV5/1000X5/100      Seq. No.: 00005     A/S Pos.: 1      Date: 01/06/93

Replicate  1                          Time: 22:06
Concentration (mg/L  ):     0.0259

Replicate  2                          Time: 22:08
Concentration (mg/L  ):     0.0258

Mean Conc  (mg/L  ):     0.0259       SD: 0.00006          RSD(%): 0.23
-------------------------------------------------------------------------------
ID: ICB                  Seq. No.: 00006     A/S Pos.: 2      Date: 01/06/93

Replicate  1                          Time: 22:10
Concentration (mg/L  ):     0.0004

Replicate  2                          Time: 22:13
Concentration (mg/L  ):     0.0001

Mean Conc  (mg/L  ):     0.0002       SD: 0.00025          RSD(%): 109.01
-------------------------------------------------------------------------------
ID: DL 0.001             Seq. No.: 00007     A/S Pos.: 3      Date: 01/06/93

Replicate  1                          Time: 22:15
Concentration (mg/L  ):     0.0010

Replicate  2                          Time: 22:17
Concentration (mg/L  ):     0.0008

Mean Conc  (mg/L  ):     0.0009       SD: 0.00013          RSD(%): 8.93
-------------------------------------------------------------------------------
ID: 222506 PB            Seq. No.: 00008     A/S Pos.: 4      Date: 01/06/93

Replicate  1                          Time: 22:21
Concentration (mg/L  ):     0.0003

Replicate  2                          Time: 22:24
Concentration (mg/L  ):     0.0002

Mean Conc  (mg/L  ):     0.0003       SD: 0.0[illegible]   RSD(%): 36.59
-------------------------------------------------------------------------------
ID: 222505 LCS           Seq. No.: 00009     A/S Pos.: 5      Date: 01/06/93

Replicate  1                          Time: 22:27
Concentration (mg/L  ):     0.0201

Replicate  2                          Time: 22:29
Concentration (mg/L  ):     0.0205

Mean Conc  (mg/L  ):     0.0203       SD: 0.0[illegible]   RSD(%): 1.65
-------------------------------------------------------------------------------
ID: 221165               Seq. No.: 00010     A/S Pos.: 6      Date: 01/06/93
```

APPENDIX
USE OF THE PE-5100 AND PE-4100 GRAPHITE FURNACES

Note: This variant of Section 3.0 works with the above Sections to form a procedure specific to the PE-5100 and PE-4100. When the steps are the same for all instruments, the procedure reads: See above (Section x.x).

3.0 GRAPHITE FURNACE PROCEDURE (PE-5100 AND PE-4100)

Note: The PE-5100 and PE-4100 use a Windows-based data system. In this procedure, the **MAIN MENU** selections at the top of the screen are indicated with bold capitals and **menu item** selections from a pull-down menu are indicated with bold lowercase.

3.1 SAMPLE PRESERVATION

See above (Section 3.1).

3.2 SAMPLE PREPARATION

See above (Section 3.2).

3.3 PRELIMINARY SET-UP

3.3.1 See above (Section 3.3), except turn on PE-5100/4100 main instrument. Ignore section 3.3.2 if running the PE-4100 because that instrument has a built-in recirculator that turns on when the instrument is turned on.

3.3.2 Verify that the correct date and time is programmed into the computer system. If not, return the system to the DOS prompt to correct these parameters before starting analysis.

3.4 DATABASE SET-UP/ELEMENT PROGRAM SELECTION

3.4.1 Double click on PE 5100.EXE icon.

3.4.2 Select **AS-60 CONTROL**. This will open a window containing a list of possible analyte elements.

3.4.3 Select the appropriate element. This will:

- bring up all of the appropriate windows on screen.
- automatically set the analytical wavelength and slit length.

Note: The slit width for Sb on the 5100 must be manually set at 0.2 mm each time this analysis is performed. The instrument will not save this value as a default slit width for Sb.

Also, if analyzing residential well samples, Sb undergoes a <u>double injection</u>: select the "SBx2" program (this repeats the first three steps

in the temperature program before atomization, doubling the sample volume and lowering the detection limit).

3.5 LAMP INSTALLATION AND ALIGNMENT

3.5.1 Open the **WINDOWS** menu.

3.5.2 Select **Align lamps**.

3.5.3 Type in the appropriate element.

3.5.4 Select and install the proper lamp for the appropriate element from Table 2B. See above (Section 3.5.1 a and b).

3.5.5 Adjust the lamp position to maximize the energy as indicated by the bar graph on the monitor. Adjust the alignment screws and slide the lamp in and out to maximize the energy reading.

3.6 FURNACE SET-UP

3.6.1 Click on **HGA Control** in the **WINDOWS** menu.

3.6.2 See above (Sections 3.6.1 - 3.6.5).

3.6.3 Click on **HGA on/off**. This will start the furnace program and take the new tube through a dry fire. If the target element is found in the tube, perform additional dry fires until the tube is free of contamination.

3.7 SAMPLE/STANDARD LOADING

See above (Section 3.7).

3.8 HGA ID/WEIGHT FILE SET-UP

Note: Because this is done after the autosampler is loaded, this serves as additional autosampler load verification.

3.8.1 Click on **ID/Weight Parameter** in the **WINDOWS** Menu.

3.8.2 Type in at the appropriate prompt the following information:

- analyst's initials.
- sample volume (1.0).
- position (1, 2, 3 ...).
- sample id (NUS Laboratory sample number).

3.8.3 Click on **Save As** in the **FILE** Menu.

3.8.4 Save the new HGA ID/Weight file in the following format:

ABBCCDDE

where A = last digit of the current year
BB = current month (2 digits)
CC = current day (2 digits)
DD = element (1 or 2 digits)
E = number of file (starts at 1 each day)

example:

A set of chromium analyses run on June 26, 1993

30626CR1

If the run is started over due to a calibration verification failure, the new file name would be 30626CR2.

3.9 CALIBRATION AND ANALYSIS

3.9.1 Perform the analytical sequence as listed in Table 5. Perform a minimum of two replicate firings for standardization, QC, and sample analyses. QC criteria are specified in Section 5.

3.9.2 Name the data file with the same file name that was saved.

3.9.3 Select **Save Data on** and **Printer on**.

3.9.4 Start the run by performing one of the following steps:

a. Select **Run Standards**. The instrument will analyze the calibration curve. If it passes quality control requirements, select **Run Samples** to complete the run.

b. Select **Run All**. The instrument will analyze the calibration curve and all samples listed in the programed sequence.

3.9.5 See above (Sections 3.8.9 - 3.8.10).

3.10 INSTRUMENT SHUT DOWN

See above (Section 3.9).

3.11 CALCULATIONS

See above (Section 3.10).

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LABORATORY METHOD

MERCURY IN WATER BY MANUAL COLD VAPOR TECHNIQUE

METHOD ID: CRA/SN-HGW
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

MERCURY IN WATER BY MANUAL COLD VAPOR TECHNIQUE

1.0 SCOPE AND APPLICATION

This method is a cold-vapor atomic absorption procedure for determining the concentration of mercury in effluents, leachates, aqueous wastes, surface waters and groundwaters. All samples must be subjected to digestion as specified in the procedure step prior to analysis. the working range for the method is 0.0002 - 0.0100 mg Hg/L.

This procedure is written for the Perkin-Elmer 50B Mercury Analyzer and utilizes software developed by NUS Laboratory for data reduction.

2.0 SUMMARY OF METHOD

The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. In addition to organic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions.

3.0 PROCEDURE

3.1 SAMPLE HANDLING AND PRESERVATION

Samples are preserved by acidification with nitric acid to a pH of 2 or lower at the time of collection. Analysis must be completed within 13 days of sample collection.

3.2 SAMPLE/STANDARD PREPARATION

3.2.1 Prepare initial calibration standards by pipetting the following aliquots of a 0.1 mg/L standard solution into 300-mL BOD bottles:

0 mL	5.0 mL
0.5 mL	7.0 mL
1.0 mL	10.0 mL
2.0 mL	

Approvals:

Technical Operations Manager	Date 4/12/94	Group Leader	Date 4/12/94	Quality Assurance Director	Date 4/12/94

Add sufficient reagent water to bring the volume to approximately 100 mL.

3.2.2 Transfer 100 mL of each sample, or an aliquot diluted to 100 mL, into 300-mL BOD bottles.

3.2.3 Prepare and analyze the following QC samples in each analytical run:

a. Duplicate/Matrix Spike: Required at a frequency of one in ten. Therefore, two duplicates and two matrix spikes are required for each batch of twenty samples.

b. Method Blank: Required at a frequency of one in twenty samples per batch. (NOTE: The ICB may be used as the method blank.)

c. Laboratory Control Sample: Required at a frequency of one in twenty samples per batch. (NOTE: The ICV may be used as the laboratory control sample.)

3.2.4 Add the following to each bottle, swirling to mix the contents thoroughly between each addition:

a. 5 mL of conc. sulfuric acid.

b. 2.5 mL of conc. nitric acid.

c. 15 mL of potassium permanganate solution

Note: If the purple color fades, add additional permanganate until the purple color persists for at least 15 minutes.

d. 8 mL of potassium persulfate solution.

3.2.5 Heat the bottles in a water bath maintained at 95 ± 1°C for 2 hours. Allow the bottles to cool.

3.3 PERKIN-ELMER MAS 50B -- INSTRUMENT SETUP

3.3.1 Mechanical Meter Zero: with the power switched OFF, make sure that the meter pointer indicates exactly 0 microgram (100%T). If it does not, adjust the meter mechanical zero adjust screw with a screwdriver to bring the meter pointer to 0 microgram (100%T).

3.3.2 Although the analyzer has been adjusted at the factory, it might become necessary to adjust it if any of the following conditions apply:

- the mercury lamp has been replaced.

- the optical filter has been replaced (should be performed ONLY by a qualified serviceman).

- when readings with standard samples constantly deviate more than five percent of full scale in one direction.

Consult the instrument manual:

- Calibration at 9.0 μg with a liquid sample, and
- Calibration at 1.0 μg with a liquid sample.

3.3.3 Plug the line cord into the power receptacle. Turn the POWER and PUMP switch ON and make sure that the pilot light glows.

3.3.4 Let the analyzer warm up for at least 15 minutes.

3.3.5 Turn the MEMORY switch OFF, the METER switch to %T, and CLOSE the shutter.

3.3.6 Turn the 0%T knob to adjust the meter pointer to approximately 0%T.

3.3.7 OPEN the shutter. Turn the 0%T knob to adjust the meter pointer to exactly 100%T. Return to 0%T by closing the shutter, and set 0%T exactly using the 0%T knob. Recheck 100%T and adjust if needed. Repeat for 0%T.

Note: If deviation is noted when opening and closing the shutter, it indicates insufficient warm up time for the lamp.

If 0%T or 100%T cannot be achieved, Hg lamp may require adjustment or cell windows may require replacement.

3.3.8 Open the shutter. Turn the METER switch to the X5 position. Fine adjust for 100%T with the 100%T knob.

3.3.9 Select the MEMORY function desired, ON or OFF. Select the %T scale.

3.4 SAMPLE AND STANDARD ANALYSIS

Perform the following steps for one bottle at a time. Analyze samples in the following sequence:

Blank
Blank
0.0005 mg/L standard
0.0010 mg/L standard
0.0020 mg/L standard
0.0050 mg/L standard

0.0070 mg/L standard
0.0100 mg/L standard
CV/LCS 1
CB/MB 1
Reporting limit standard
Sample 1
Sample 1 DUP
Sample 1 MS
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
Sample 8
Sample 9
Sample 10
CV/LCS 2
CB/MB 2
Sample 11
Sample 11 DUP
Sample 11 MS
Sample 12
Sample 13
Sample 14
Sample 15
Sample 16
Sample 17
Sample 18
Sample 19
Sample 20
CV/LCS 3
CB/MB 3

Repeat the sequence of ten samples, CV/LCS & CB/MB, until all samples are analyzed.

CV/LCS n
CB/MB n

3.4.1 Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

Note: This step may release toxic chlorine gas.

3.4.2 When the solution has decolorized, wait 30 seconds, then add 5 mL of stannous sulfate solution and immediately attach the bottle to the aeration tube.

Stannous chloride volatilizes the mercury. It is, therefore, essential that this step is performed very rapidly.

3.4.3 Observe the transmittance reading decrease on the meter to a minimum point.

3.4.4 When the reading levels off (at approximately 1 minute), record the reading in the analysis log.

3.4.5 Open the bypass valve and continue aeration until transmittance returns to its maximum value.

3.4.6 Close the bypass valve, remove the stopper and frit from the bottle, and rinse them with reagent water. Continue aeration.

3.5 DATA REDUCTION

3.5.1 Enter mercury standard concentrations and corresponding percent transmittance values into the mercury software program.

3.5.2 After all standard points have been entered, save the data using the SAVE DATA TO DISK option.

3.5.3 Print the calibration data (standard concentration, absorbance) using the PRINT DATA option.

3.5.4 Calculate the correlation coefficient of the calibration curve using the RUN CORRELATION PROGRAM option. The correlation coefficient must be ≥ 0.995.

3.5.5 Calculate sample concentrations from the calibration curve using the RUN CORRELATION PROGRAM option. Manually correct concentration values obtained from the software program for dilutions using the following formula:

$$mg/L\ Hg = mg/L\ Hg\ (from\ curve) \times \frac{100mL}{sample\ volume\ (mL)}$$

3.5.6 Plot the calibration curve using the RUN PLOT PROGRAM option.

4.0 DATA COLLECTION

4.1 Document the following in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. See Figure 1.

Data collection should include the following:

- analysis method root code (i.e., AHGBO, AHGS, or AHGW) and brief

description.

- date and time analysis started and analyst(s) signature(s).
- NUS Laboratory sample number and sample aliquot. Identify any lab quality control samples (method blanks, DUP/MS, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added for post-digestion spikes.

4.2 Forward the following to data management from each analytical run:

- preparation/analytical raw data, including logbook page(s), worksheet/assignment sheets, and standard preparation pages.
- description of problems encountered and actions taken during sample preparation and analysis on corrective action records.
- any instrument maintenance documented in the instrument maintenance log.

5.0 QUALITY CONTROL

5.1 INSTRUMENT CALIBRATION

Prepare and analyze two blanks and standards at 6 concentration levels at the start of each analytical sequence each time samples are prepared. Include the instrument standardization date and time in the raw data.

5.2 CALIBRATION VERIFICATION/LABORATORY CONTROL SAMPLE (CV/LCS)

Immediately after initial instrument calibration, every 10 samples, and at the end of each analytical sequence, verify the accuracy of the initial calibration and the efficiency of the overall digestion procedure by preparing and analyzing an aqueous CV/LCS. This standard is independent of the calibration standards.

Recovery limits for the LCS are listed in Table 1. The LCS limits are statistically based and are updated annually; they are subject to change.

If results for the aqueous CV/LCS fall outside the control limits, terminate the analysis, correct the problem, then redigest and reanalyze all samples and standards in the batch.

5.3 CALIBRATION BLANK/METHOD BLANK (CB/MB)

Immediately analyze a CB/MB after each CV/LCS, at a frequency of every ten samples. The blank must be analyzed at the beginning of the run and after the last CV/LCS that was run after the last sample of the run.

Evaluate CB/MB results as follows:

5.3.1 If the absolute value of the concentration of the blank is less than or equal to the reporting limit, do not correct the results.

5.3.2 If any analyte concentration in the blank is above the reporting limits, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the reporting limit, must be reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.

5.3.3 If the concentration of the blank is below the negative reporting limit, then all samples reported below 10x the reporting limit associated with the blank must be redigested and reanalyzed.

5.4 REPORTING LIMIT (RL) STANDARD

The reporting limit standard is a standard analyzed at the concentration of the reporting limit. Run an RL immediately after the initial CB/MB. The RL has a recovery criterion of $\geq$ 50%. If this limit is not met, terminate the analysis sequence; troubleshoot the standard solution, digestion, and/or CVAA system; redigest the batch.

An acceptable reporting limit standard recovery must be obtained prior to continuing sample analysis.

5.5 SPIKE SAMPLE ANALYSIS

The spike sample analysis is designed to provide information about the effects of the sample matrix on the digestion and measurement methodology.

Add 1 µg/L spike at the start of sample preparation, and prior to the addition of other reagents, to a second aliquot of the selected sample(s). At least one spike sample analysis must be performed for every ten samples digested together.

If the spike recovery is not at or within the limits of 75-125%, the data for that sample is flagged. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

Percent recovery (%R) is calculated as follows:

$$\%\ Recovery = \frac{(SSR - SR)}{SA} \times 100$$

where ***SSR*** = Spiked Sample Result
SR = Sample Result
SA = Spike Added

When the sample concentration is less than the reporting limit, use SR = 0 for purposes of calculating % Recovery.

5.6 DUPLICATE SAMPLE ANALYSIS

Analyze one sample in duplicate for every ten samples digested together. The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

where ***RPD*** = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

Limits for precision are listed in Table 1. If range or RPD exceeds the acceptance limits for an aqueous sample matrix, reanalyze the duplicate sample. If precision remains non-conforming, redigest and reanalyze the original and duplicate samples and 25% of the positive results.

Note: If 25% of positive samples does not calculate to a whole number, round up to determine the number of samples to be rerun.

If reanalysis results do not duplicate original results, redigest and reanalyze all samples and report reanalysis results.

5.7 INSTRUMENT DETECTION LIMIT (IDL) DETERMINATION

Determine instrument detection limits for each instrument used, at least quarterly (every 3 calendar months). The IDLs must meet the reporting limits.

Determine the Instrument Detection Limits as follows:

- Prepare a standard solution at a concentration 3-5x the manufacturer's suggested IDL initially, then 3-5x the previously determined IDL thereafter.

- Perform seven consecutive measurements of the standard on three nonconsecutive days (a total of 21 measurements).

  Perform each measurement as if it were a separate analytical sample followed by a rinse and/or any other procedure normally performed between analyses of separate samples.

  Calculate the mean and standard deviation for each set of seven

measurements. The observed daily mean must fall within a factor of two of the true value for the data to be useful for the IDL study.

- Average the standard deviation values.
- Calculate the IDL (μg/L) by multiplying the average SD by 3.

IDLs are determined and reported.

If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

5.8 METHOD DETECTION LIMIT STUDIES

A method detection limit (MDL) study for water analysis is performed annually according to 40 CFR 136, Appendix B. Statistically-based MDLs must be $\leq$ reporting limits for the method.

6.0 INTERFERENCES

6.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

6.2 Cooper has also been reported to interfere; however, cooper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

6.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

6.4 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EPA's EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility.

7.0 SAFETY PRECAUTIONS

7.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

7.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.2 Handle and store all reagents in accordance with the precautions listed on the Material Safety Data Sheets (MSDS).

7.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.4 Handle all glass equipment with care.

7.5 When preparing diluted solutions of concentrated acids, ALWAYS ADD ACID to WATER.

7.6 An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

7.7 Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, 0.25% iodine in a 3% KI solution, or s specially treated charcoal that will absorb mercury vapor.

8.0 APPARATUS AND MATERIALS

8.1 Perkin-Elmer 50B or Bacharach/Coleman MAS50B Mercury Analyzer.

8.2 Software program for calculation of mercury results.

9.0 REAGENTS

The toxicity or carcinogenicity of each reagent used in this method has not been

precisely defined; however, each chemical compound should be treated as a potential health hazard. A reference file of Material Safety Data Sheets is available to all personnel.

9.1 Reagent water: Deionized water.

9.2 Sulfuric acid, concentrated: reagent grade of low mercury content.

9.3 Sulfuric acid, 0.5N: dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.

9.4 Nitric acid, concentrated: reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

9.5 Stannous sulfate: add 25 g of stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

9.6 Sodium chloride-hydroxylamine sulfate solution: dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

9.7 Potassium permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

9.8 Potassium persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of reagent water.

9.9 Stock mercury solution (1 mL = 1 mg Hg): dissolve 0.1354 g of mercuric chloride in 75 mL if reagent water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. Stock solutions may also be purchased.

9.10 Working mercury solution: make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

10.0 REFERENCES

10.1 U.S. EPA. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, revised March, 1983. Method 245.1.

10.2 U.S. EPA. "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods," SW-846, 1986. Method 7470.

TABLE 1

QUALITY CONTROL TEST FILE - METALS
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	x̄	s	RPD Cpk[1]	Warning Limits for % LCS Recovery	Control Limits for LCS Recovery	x̄	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	x̄	s
00, Mercury 50B, Water	CA07	Range: --- RPD: ≤9.01%	Range: ≤2X IDL RPD: ≤12.6%	1.91	3.55	0.76	86.0-114	79.0-121	100.00	7.01	0.95	77.1-133	63.1-147	105.12	13.99
00, Mercury 50B, Solid	CA06	Range: --- RPD: ≤14.3%	Range: ≤4X IDL RPD: ≤19.2%	4.46	4.90	1.06	68.6-128	53.1-150	98.08	14.73	0.52	56.3-142	34.8-164	99.31	21.52
00, Mercury, M50B, Water	CA09	Range: --- RPD: ≤13.1%	Range: ≤2X IDL RPD: ≤17.7%	3.80	4.63	0.45	86.4-109	80.7-115	97.93	5.74	1.04	78.0-134	64.0-148	105.94	13.98
00, Mercury	CA05	Range: --- RPD: ≤21.3%	Range: ≤4X IDL RPD: ≤28.5%	7.04	7.15	0.60	72.0-132	53.1-150	102.04	15.03	0.51	66.2-146	45.2-166	106.30	20.03

PM = preparation method
x̄ = mean
s = standard deviation
LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit
[1] Cpk based on 10% RPD specification goal.
[2] Cpk based on 80-120% recovery specification goal.

FIGURE 1

TITLE AM-AHGW

Mercury in Water by CVAA

PROJECT NO.

BOOK NO. P140-92

230

EXAMPLE

Work continued from Page

Instrument: MAS 508
Run Start Time: 0900
Wavelength: 253.7nm
Filename: bg920514
Calibration Standards Reference:
Blank: 8-260-92-280
0.0005 mg/L: 4-260-92-280
0.0010 mg/L: 5-260-92-280
0.0020 mg/L: 6-260-92-280
0.0050 mg/L: 7-260-92-280
0.0100 mg/L: 8-260-92-280

Initial Calibration Verification
Prep. Reference: 9-260-92-280
Source: SPEX WP15
Lot No.: 3-97AS
True Value: 5.1 mg/L
Continuing Calibration Verification
Prep Reference: 9-260-92-280
Source: SPEX WP15
Lot No.: 3-97AS
True Value: 5.1 mg/L
Matrix Spike Prep. Reference:
Add 1.0 ml of 0.1 mg/L std
Ref: 1-260-92-280

	Sample ID	Bottle ID	Aliq. (ml)	Diln.	%T	Absorbance	Concentration (mg/L)	Result (mg/L)	Comments
	Blank	A			100.0				
	S-0.0005	B			96.0				
	S-0.0010	C			91.0				
	S-0.0020	D			82.0				
	S-0.0050	E			60.0				
	S-0.0100	F							
	Blank	G	100		100.0				
	ICV/LCSR	H	5	100	78.0	0.107905	0.002520	5.04	98.8% R
	ICB/PB	I	100		100.0	-0.000000	0.000012	<0.0002	
Sx 1	199255	J	100		98.0	0.008774	0.000216	0.0002	(0.00022)
	199255-DUP	K	100		97.5	0.009995	0.000247	0.00027	Range = 0.00005
	199255-MS	L	100		89.5	0.048177	0.001132	0.00113	MSR = 91.0%
	198855	M	100		98.5	0.006564	0.000164	<0.0002	
	198856	N	100		100.0	-0.000000	0.000012	<0.0002	
Sx 10	199286	S	100		100.0	-0.000000	0.000012	<0.0002	
	CCV-1	T	5	100	78.5	0.105130	0.002456	4.91	96.3% R
	CCB-1	V	100		100.0	-0.000000	0.000012	<0.0002	

Work continued to Page

SIGNATURE John C. Doe | DATE 7/22/92

DISCLOSED TO AND UNDERSTOOD BY | DATE | WITNESS | DATE

FIGURE 2

TITLE — PROJECT NO. 280 — BOOK NO. P260-92

Work continued from Page

Mercury Standards: — EXAMPLE —

Stock: Johnson Matthey AA Mercury Standard
Concentration: 1000 mg/L
Lot No.: I-008LII

SOLN I	10.0 mg/L : 5.0 mL Stock / 500 mL EV	1-260-92-280
SOLN II	0.1 mg/L : 10.0 mL 1-260-92-280 / 1000 mL EV	2-260-92-280
SOLN III	0.01 mg/L : 20.0 mL 2-260-92-280 / 200 mL EV	3-260-92-280
	0.0005 mg/L : 5.0 mL 3-260-92-280 / 100 mL EV	4-260-92-280
	0.0010 mg/L : 10.0 mL 3-260-92-280 / 100 mL EV	5-260-92-280
	0.0020 mg/L : 20.0 mL 3-260-92-280 / 100 mL EV	6-260-92-280
	0.0050 mg/L : 5.0 mL 2-260-92-280 / 100 mL EV	7-260-92-280
	Blank : DI Water	8-260-92-280

All standard solutions contain 1% HNO_3

Prepared : 7/22/92 1125AM
By : JCD

Initial/Continuing Calibration Verification and ICS

Stock: SPEX WP15
Concentration: 5.1 mg/L
Lot No.: 3-97AS

2.0 mL Stock / 200 mL EV — 9-260-92-280
Conc = 0.051 mg/L

Standard solution contains 1% HNO_3

Prepared : 7/22/92 1135AM
By : JCD

Work continued to Page

SIGNATURE — DATE

DISCLOSED TO AND UNDERSTOOD BY — DATE — WITNESS — DATE

FIGURE 3

MERCURY
STANDARD CURVE

-EXAMPLE-

Date: 7/22/92

Analyst: cfk

Stock Solution - 1000 mg/L Hg

Instrument: Perkin-Elmer 50B

Manufacturer: Johnson-Matthey

Wavelength: 253.7 nm

Lot #: 1-0081 I

Digestion: Autoclave: _____

SOLUTION I - 10 mg/l Hg

Steam Bath:

10.0 mL STOCK SOLN plus 5 mL HNO_3/1 Liter

Time On 12.00 Temp (°C) 95.0

SOLUTION II - 0.1 mg/L Hg

Time 1230 Temp (°C) 95.5

10.0 mL SOLN I plus 5 mL HNO_3/1 Liter

Time 1300 Temp (°C) 95.5

SOLUTION III - 0.01 mg/L Hg

Time 1330 Temp (°C) 95.0

10.0 mL SOLN II plus 0.5 mL HNO_3/100 mL

Time _____ Temp (°C) _____

Time Off 1400 Temp (°C) 95.0

Final Dilution	Final Conc.	Peak Height (T%)
0.0 mL	0.0000 mg/L	100.0
5.0 mL SOLN III/100 mL	0.0005 mg/L	96.0
10.0 mL SOLN III/100 mL	0.0010 mg/L	91.0
2.0 mL SOLN II/100 mL	0.0020 mg/L	82.0
5.0 mL SOLN II/100 mL	0.0050 mg/L	60.0
10.0 mL SOLN II/100 mL	0.0100 mg/L	37.5
0.0 mL	0.0000 mg/L	100.0

Correlation Coefficient (r): 0.9997034

CALCULATIONS:

$$Absorbance = 2 - \log (\%T)$$

$$mg/L\ Hg = (Curve\ Reading)\left(\frac{100\ mL}{Sample\ Aliquot}\right)(Dilutions)$$

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LABORATORY METHOD

MERCURY IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

METHOD ID: CRA/SN-HGS
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

MERCURY IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

1.0 SCOPE AND APPLICATION

This method measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge-type materials. The range of the method is 0.2 to 5 μg/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument control.

This procedure is written for the Perkin-Elmer and Bacharach/Coleman MAS Mercury Analyzers and utilizes software developed by NUS Laboratory for data reduction.

2.0 SUMMARY OF METHOD

A weighed portion of the sample is digested with aqua regia, potassium permanganate, and heat. Mercury in the digested sample is then measured by the conventional cold vapor technique.

3.0 PROCEDURE

3.1 SAMPLE HANDLING AND PRESERVATION

3.1.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, take care to avoid extraneous contamination. Wash glassware carefully.

3.1.2 Refrigerate solid samples at 4°C (±2°C) upon receipt until analysis.

3.1.3 Analyze the sample without drying.

3.2 CALIBRATION AND SAMPLE ANALYSIS

3.2.1 Prepare the standards, samples, and quality control checks as described below. Quality control checks are also described in Section 5.0.

a. Initial calibration: Transfer 0.0, 2.0, 5.0, and 10.0 mL aliquots of a 0.01 μg/mL mercury standard to a series of 300-mL BOD bottles.

Approvals:

Charles A Kiesa 4/12/94
Technical Operations Manager — Date

Jonathan Talbott 4/12/94
Group Leader — Date

Lisa Mey 4/12/94
Quality Assurance Director — Date

Add sufficient reagent water to each bottle to bring the volume to approximately 10 mL.

b. Continuing calibration blanks (CCB): Transfer 10 mL of reagent water to a BOD bottle for each blank.

c. Initial calibration verification (ICV) standard: Transfer a known volume of an independent standard containing 0.05 - 1.0 μ Hg into a BOD bottle for each standard. Dilute to 10 mL with reagent water.

d. Continuing calibration verification (CCV) standards: Transfer a known volume of the 0.1 μg/mL mercury working standard containing 0.05 - 1.0 μg Hg to a BOD bottle for each standard. Dilute to 10 mL with reagent water.

e. Laboratory control sample (LCS): Weigh a 0.2 g portion of solid reference material, or appropriate aliquot to bring within linear range, to the nearest 0.0001 g and quantitatively transfer it to the bottom of a BOD bottle.

f. Each sample: Weigh a representative 0.2 g portion of wet sample to the nearest 0.0001 g and quantitatively transfer it to the bottom of a BOD bottle. (Use a smaller aliquot if a 0.2 aliquot exceeds the linear range of the analyzer.)

g. Duplicate: Weigh a second 0.2 g aliquot of 1 in 10 samples being prepared together and quantitatively transfer it to the bottom of a BOD bottle.

h. Matrix spike: Weigh a third 0.2 g aliquot of 1 in 10 samples being prepared together and quantitatively transfer it to the bottom of a BOD bottle. Add 2.0 mL of the 0.1 μg/mL mercury working standard to the bottle.

3.2.2 Add 5 mL of aqua regia to each bottle and swirl. Heat samples for 2 minutes in a water bath maintained at 95°C. Remove the samples from the water bath and cool.

3.2.3 Add 50 mL of reagent water and 15 mL of $KMnO_4$ solution to each bottle. Observe the samples for several minutes. If the purple color fades, add additional $KMnO_4$ solution. Continue additions until the purple color remains for several minutes.

3.2.4 Add 8 mL of potassium persulfate solution and return the bottle to the water bath for 30 minutes. Remove the samples from the water bath and cool.

3.2.5 Add 50 mL of reagent water to each bottle.

3.2.6 An alternate digestion procedure employing an autoclave may also be used. Weigh a representative 0.2 g portion of wet sample to the nearest 0.0001 g and quantitatively transfer it to the bottom of a BOD bottle. Add 5 mL of concentrated sulfuric acid and 2 mL of concentrated nitric acid to the sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. Autoclave the sample at 121°C and 15 lbs. for 15 minutes.

Cool, increase the volume to 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate.

3.3 PERKIN-ELMER MAS 50B -- INSTRUMENT SETUP

3.3.1 Mechanical Meter Zero: with the power switched OFF, make sure that the meter pointer indicates exactly 0 microgram (100%T). If it does not, adjust the meter mechanical zero adjust screw with a screwdriver to bring the meter pointer to 0 microgram (100%T).

3.3.2 Although the analyzer has been adjusted at the factory, it might become necessary to adjust it if any of the following conditions apply:

- the mercury lamp has been replaced.
- the optical filter has been replaced (should be performed ONLY by a qualified serviceman).
- when readings with standard samples constantly deviate more than five percent of full scale in one direction.

Consult the instrument manual:

- Calibration at 9.0 μg with a liquid sample, and
- Calibration at 1.0 μg with a liquid sample.

3.3.3 Plug the line cord into the power receptacle. Turn the POWER and PUMP switch ON and make sure that the pilot light glows.

3.3.4 Let the analyzer warm up for at least 15 minutes.

3.3.5 Turn the MEMORY switch OFF, the METER switch to %T, and CLOSE the shutter.

3.3.6 Turn the 0%T knob to adjust the meter pointer to approximately 0%T.

3.3.7 OPEN the shutter. Turn the 0%T knob to adjust the meter pointer to exactly 100%T. Return to 0%T by closing the shutter, and set 0%T exactly using the 0%T knob. Recheck 100%T and adjust if needed.

Repeat for 0%T.

Note: If deviation is noted when opening and closing the shutter, it indicates insufficient warm up time for the lamp.

If 0%T or 100%T cannot be achieved, Hg lamp may require adjustment or cell windows may require replacement.

3.3.8 Open the shutter. Turn the METER switch to the X5 position. Fine adjust for 100%T with the 100%T knob.

3.3.9 Select the MEMORY function desired, ON or OFF. Select the %T scale.

3.4 SAMPLE AND STANDARD ANALYSIS

Perform the following steps for one bottle at a time. Analyze samples in the following sequence:

Blank
Blank
0.0005 mg/L standard
0.0010 mg/L standard
0.0020 mg/L standard
0.0050 mg/L standard
0.0070 mg/L standard
0.0100 mg/L standard
ICV
ICB
Reporting limit standard
LCS
Method blank
Sample 1
Sample 1 DUP
Sample 1 MS
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
Sample 8
Sample 9
Sample 10
CCS 1
CCB 1
Sample 11
Sample 11 DUP
Sample 11 MS

Sample 12
Sample 13
Sample 14
Sample 15
Sample 16
Sample 17
Sample 18
Sample 19
Sample 20
CCS 2
CCB 2

Repeat the sequence of twenty samples, LCS, method blank, CCS, and CCB until all samples are analyzed.

CCS n
CCB n

3.4.1 Under an operating fume hood, add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

Note: This step may release toxic chlorine gas.

3.4.2 When the solution has decolorized, wait 30 seconds, then add 5 mL of stannous sulfate solution and immediately attach the bottle to the aeration tube.

Stannous chloride volatilizes the mercury. It is, therefore, essential that this step is performed very rapidly.

3.4.3 Observe the transmittance reading decrease on the meter to a minimum point.

3.4.4 When the reading levels off (at approximately 1 minute), record the reading in the analysis log.

3.4.5 Open the bypass valve and continue aeration until transmittance returns to its maximum value.

3.4.6 Close the bypass valve, remove the stopper and frit from the bottle, and rinse them with reagent water. Continue aeration.

3.5 DATA REDUCTION

3.5.1 Enter mercury standard concentrations and corresponding percent transmittance values into the mercury software program.

3.5.2 After all standard points have been entered, save the data using the

SAVE DATA TO DISK option.

3.5.3 Print the calibration data (standard concentration, absorbance) using the PRINT DATA option.

3.5.4 Calculate the correlation coefficient of the calibration curve using the RUN CORRELATION PROGRAM option. The correlation coefficient must be ≥ 0.995.

3.5.5 Calculate sample concentrations from the calibration curve using the RUN CORRELATION PROGRAM option. Manually correct concentration values obtained from the software program for dilutions using the following formula:

$$mg/kg\ Hg = mg/kg\ Hg\ (from\ curve) \times \frac{100mL}{sample\ volume\ (mL)} \times \frac{1000\ g}{kg}$$

3.5.6 Plot the calibration curve using the RUN PLOT PROGRAM option.

4.0 DATA COLLECTION

4.1 Document the following in a bound lab notebook for each set of analyses performed. Entries must be made at the time of analysis. See Figure 1.

Data collection should include the following:

- analysis method root code (i.e., AHGBO, AHGS, or AHGW) and brief description.
- date and time analysis started and analyst(s) signature(s).
- NUS Laboratory sample number and sample aliquot. Identify any lab quality control samples (method blanks, DUP/MS, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added for post-digestion spikes.

4.2 Forward the following to data management from each analytical run:

- preparation/analytical raw data, including logbook page(s), worksheet/assignment sheets, and standard preparation pages.
- description of problems encountered and actions taken during sample preparation and analysis on corrective action records.
- any instrument maintenance documented in the instrument maintenance log.

5.0 QUALITY CONTROL

5.1 INSTRUMENT CALIBRATION

Prepare and analyze two blanks and standards at 6 concentration levels at the start of each analytical sequence each time samples are prepared. Include the instrument standardization date and time in the raw data.

5.2 INITIAL CALIBRATION VERIFICATION (ICV)

Immediately after initial instrument calibration, verify the accuracy of the initial calibration and the efficiency of the overall digestion procedure by preparing and analyzing an aqueous ICV for each batch of soil samples digested together. This standard is independent of the calibration standards. When measurements exceed the control limits of 80.0 - 120%, terminate analysis, correct the problem, reprepare samples, and repeat calibration.

5.3 CONTINUING CALIBRATION STANDARD (CCS)

To ensure calibration accuracy during each analysis run, analyze a continuing calibration verification after every ten samples. The standard must also be analyze after the last sample. Each CCS must reflect the conditions of analysis of all associated samples (the preceding 10 samples or the preceding samples up to the previous CCS).

If the recovery of the continuing calibration verification is outside the control limits of 80.0 - 120%, terminate the analysis, correct the problem, then redigest and reanalyze either the preceding 10 samples or all samples analyzed since the last good calibration verification.

5.4 INITIAL CALIBRATION BLANK (ICB) AND CONTINUING CALIBRATION BLANK (CCB)

Immediately analyze a calibration blank after ever initial and continuing calibration verification, at a frequency of every ten samples. The blank must be analyzed at the beginning of the run and after the last CCV that was run after the last sample of the run.

Evaluate blank (ICB, CCB) results as follows:

5.4.1 If the absolute value of the concentration of the blank is less than or equal to the reporting limit, do not correct the results.

5.4.2 If any analyte concentration in the blank is above the reporting limits, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the reporting limit, must be reanalyzed for that

analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.

5.4.3 If the concentration of the blank is below the negative reporting limit, then all samples reported below 10x the reporting limit associated with the blank must be redigested and reanalyzed.

5.5 REPORTING LIMIT (RL) STANDARD

The reporting limit standard is a standard analyzed at the concentration of the reporting limit. Run an RL immediately after the initial CB/MB. The RL has a recovery criterion of $\geq$ 50%. If this limit is not met, terminate the analysis sequence; troubleshoot the standard solution, digestion, and/or CVAA system; redigest the batch.

An acceptable reporting limit standard recovery must be obtained prior to continuing sample analysis.

5.6 LABORATORY CONTROL SAMPLE (LCS)

Prepare and analyze one solid LCS for each batch of up to twenty solid samples digested together.

Recovery limits for the LCS are listed in Table 1. The LCS limits are statistically based and are updated annually; they are subject to change.

5.7 METHOD BLANK

The method blank is an empty BOD bottle to which all reagents are added and all manipulations are performed. Prepare and analyze one method blank for each batch of up to 20 solid samples digested together. The method blank must be below the reporting limit. If it is not, troubleshoot the system and redigest all samples associated with the blank that are > the reporting limit and $\leq$ 10x the level in the blank.

5.8 SPIKE SAMPLE ANALYSIS

The spike sample analysis is designed to provide information about the effects of the sample matrix on the digestion and measurement methodology.

Add 1 μg/L spike at the start of sample preparation, and prior to the addition of other reagents, to a second aliquot of the selected sample(s). At least one spike sample analysis must be performed for every ten samples digested together.

If the spike recovery is not at or within the limits of 75-125%, the data for that sample is flagged. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four

or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

Percent recovery (%R) is calculated as follows:

$$\%\ Recovery = \frac{(SSR - SR)}{SA} \times 100$$

where SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

When the sample concentration is less than the reporting limit, use SR = 0 for purposes of calculating % Recovery.

5.9 DUPLICATE SAMPLE ANALYSIS

Analyze one sample in duplicate for every ten samples digested together. The relative percent difference (RPD) is calculated as follows:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

where RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

Limits for precision are listed in Table 1. If range or RPD exceeds the acceptance limits for an aqueous sample matrix, reanalyze the duplicate sample. If precision remains non-conforming, redigest and reanalyze the original and duplicate samples and 25% of the positive results.

Note: If 25% of positive samples does not calculate to a whole number, round up to determine the number of samples to be rerun.

If reanalysis results do not duplicate original results, redigest and reanalyze all samples and report reanalysis results.

5.10 INSTRUMENT DETECTION LIMIT (IDL) DETERMINATION

Determine instrument detection limits for each instrument used, at least quarterly (every 3 calendar months). The IDLs must meet the reporting limits.

Determine the Instrument Detection Limits as follows:

- Prepare a standard solution at a concentration 3-5x the manufacturer's suggested IDL initially, then 3-5x the previously determined IDL thereafter.

- Perform seven consecutive measurements of the standard on three nonconsecutive days (a total of 21 measurements).

  Perform each measurement as if it were a separate analytical sample followed by a rinse and/or any other procedure normally performed between analyses of separate samples.

  Calculate the mean and standard deviation for each set of seven measurements. The observed daily mean must fall within a factor of two of the true value for the data to be useful for the IDL study.

  - Average the standard deviation values.
  - Calculate the IDL (μg/L) by multiplying the average SD by 3.

  IDLs are determined and reported.

  If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

5.10 METHOD DETECTION LIMIT STUDIES

A method detection limit (MDL) study for water analysis is performed annually according to 40 CFR 136, Appendix B. Statistically-based MDLs must be $\leq$ reporting limits for the method.

6.0 INTERFERENCES

6.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

6.2 Cooper has also been reported to interfere; however, cooper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

6.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

6.4 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EPA's EMSL has not encountered such

samples. This is mentioned only to caution the analyst of the possibility.

6.5 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic material will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in digestion.

7.0 SAFETY PRECAUTIONS

7.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

7.1.1 Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.2 Handle and store all reagents in accordance with the precautions listed on the Material Safety Data Sheets (MSDS).

7.2.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.2.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.2.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.3 Avoid breathing solvent and standard solution vapors. If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.4 Handle all glass equipment with care.

7.5 When preparing diluted solutions of concentrated acids, ALWAYS ADD ACID to WATER.

7.6 An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

7.7 Because of the toxic nature of mercury vapor, precaution must be taken to avoid inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, 0.25% iodine in a 3% KI solution, or s specially treated charcoal that will absorb mercury vapor.

8.0 APPARATUS AND MATERIALS

8.1 Perkin-Elmer 50B or Bacharach/Coleman MAS 50B Mercury Analyzer.

8.2 Software program for calculation of mercury results.

9.0 REAGENTS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. A reference file of Material Safety Data Sheets is available to all personnel.

9.1 Reagent water: deionized water.

9.2 Aqua regia: prepare immediately before use by carefully adding three volumes of concentrated hydrochloric acid to one volume of concentrated nitric acid.

9.3 Sulfuric acid, 0.5N: dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.

9.4 Stannous sulfate: add 25 g of stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

9.5 Sodium chloride-hydroxylamine sulfate solution: dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

9.6 Potassium permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

9.7 Potassium persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of reagent water.

9.8 Stock mercury solution (1 mL = 1 mg Hg): dissolve 0.1354 g of mercuric chloride in 75 mL if reagent water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. Stock solutions may also be purchased.

9.9 Working mercury solution: make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg per mL. This working

standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

10.0 REFERENCES

10.1 U.S. EPA. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, revised March, 1983. Method 245.5.

10.2 U.S. EPA. "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods," SW-846, 1986. Method 7471.

TABLE 1

QUALITY CONTROL TEST FILE - METALS
November 1993

PM, Analyte	Comb. ID	Warning Limits for Precision	Control Limits for Precision	$\bar{x}_R$	s_R	RPD Cpk[1]	Warning Limits for LCS Recovery	Control Limits for LCS Recovery	$\bar{x}$	s	LCS Cpk[2]	95% CI for Matrix Spike Recovery	99% CI for Matrix Spike Recovery	$\bar{x}$	s
00, Mercury 50B, Water	CA07	Range: --- RPD: ≤9.01%	Range: ≤2X IDL RPD: ≤12.6%	1.91	3.55	0.76	86.0-114	79.0-121	100.00	7.01	0.95	77.1-133	63.1-147	105.12	13.99
00, Mercury 50B, Solid	CA06	Range: --- RPD: ≤14.3%	Range: ≤4X IDL RPD: ≤19.2%	4.46	4.90	1.06	68.6-128	53.1-150	98.08	14.73	0.52	56.3-142	34.8-164	99.31	21.52
00, Mercury, M50B, Water	CA09	Range: --- RPD: ≤13.1%	Range: ≤2X IDL RPD: ≤17.7%	3.80	4.63	0.45	86.4-109	80.7-115	97.93	5.74	1.04	78.0-134	64.0-148	105.94	13.98
00, Mercury	CA08	Range: --- RPD: ≤21.3%	Range: ≤4X IDL RPD: ≤28.5%	7.04	7.15	0.60	72.0-132	53.1-150	102.04	15.03	0.51	66.2-146	46.2-166	106.30	20.03

PM = preparation method
$\bar{x}$ = mean
s = standard deviation
LCS = lab control standard
CI = confidence interval
IDL = instrument detection limit
[1] Cpk based on 10% RPD specification goal.
[2] Cpk based on 80-120% recovery specification goal.

FIGURE 1

TITLE

PROJECT NO. 18

BOOK NO. P260-92

Work continued from Page

DUPLICATE

Mercury Standards:

Stock: Johnson Matthey AA Mercury Standard
Concentration: 1000 mg/L
Lot No. I-00811

SOLN I	10.0 mg/L :	5.0 mL stock / 500 mL FV	1-260-92-18
SOLN II	0.1 mg/L :	10.0 mL 1-260-92-18 / 1000 mL FV	2-260-92-18
	0.01 mg/L :	20.0 mL 2-260-92-18 / 200 mL FV	3-260-92-18
	0.0005 mg/L :	5.0 mL 3-260-92-18 / 100 mL FV	4-260-92-18
	0.0010 mg/L :	10.0 mL 3-260-92-18 / 100 mL FV	5-260-92-18
	0.0020 mg/L :	20.0 mL 3-260-92-18 / 100 mL FV	6-260-92-18
	0.0050 mg/L :	5.0 mL 2-260-92-18 / 100 mL FV	7-260-92-18
	Blank :	DI Water	8-260-92-18

All standard solutions contain 1% HNO_3

Prepared: 10/26/92, 1050
By: JCD

Initial/Continuing Calibration Verification

Stock: SPEX WP 15
Concentration: 5.1 mg/L
Lot No: 3-97AS

2.0 mL stock / 200 mL FV 9-260-92-18
Conc = 0.051 mg/L

Standard solution contains 1% HNO_3

Prepared: 10/26/92 1100
By: JCD

Work continued to Page

SIGNATURE DATE

DISCLOSED TO AND UNDERSTOOD BY DATE WITNESS DATE

FIGURE 2

TITLE AM: AHGS PROJECT NO. 118

BOOK NO. P140-92

Mercury in Soil by CVAA

Work continued from Page — DUPLICATE

Instrument: MAS50B
Run Start Time: 1030
Wavelength: 253.7nm
Filename: hg921026
Calibration Standards Reference:
Blank: 8-260-92-18
0.0005 mg/L: 4-260-92-18
0.0010 mg/L: 5-260-92-18
0.0020 mg/L: 6-260-92-18
0.0050 mg/L: 7-260-92-18
0.0100 mg/L: 3-260-92-18
Waterbath: Time 1230 Temp 95.0
Time 1300 Temp 95.0
Time 1330 Temp 95.0

Initial Calibration Verification
Prep Reference: 9-260-92-18
Source: SPEX WP15
Lot No.: 3-97AS
True Value: 5.1 mg/L
Continuing Calibration Verification
Prep Reference: 9-260-92-18
Source: SPEX WP15
Lot No.: 3-97AS
True Value: 5.1 mg/L
Matrix Spike Prep Reference
Add 2.0 ml of 0.1 mg/L std
Ref 2-260-92-18
LCSR: ERA Lot No 211

Sample ID	Bottle ID	Aliq (g)	Aliq (ml)	Dilu	%T	Result mg/L	Comments
Blank	A				100.0		
S-0.0005	B				96.5		
S-0.0010	C				93.5		
S-0.0020	D				85.0		
S-0.0050	E				68.0		
S-0.0100	F				48.0		
Blank	G		100		100.0	<0.0002	
ICV	H		5	100	83.0	4.96	97.3% R
ICB/PB	I	0.2000	100		100.0	<0.0002	
LCSR	J	0.0534			65.5		
214543	K	0.2113			84.0		
214543DUP	L	0.2098			83.0		
214543MS	M	0.2108			72.0		
214546	W	0.2007			99.0		
CCV-1	X		5	100	82.5	5.13	101% R
CCB-1	Y		100		100.0	<0.0002	

Work continued to Page

SIGNATURE John C. Doe DATE 10/26/92

DISCLOSED TO AND UNDERSTOOD BY | DATE | WITNESS | DATE

FIGURE 3

MERCURY
STANDARD CURVE

Date: _____

Analyst: _____

Stock Solution - 1000 mg/L Hg

Instrument: _____

Manufacturer: _____

Wavelength: 253.7 nm

Lot #: _____

Digestion: Autoclave: _____

SOLUTION I - 10 mg/l Hg

Steam Bath:

10.0 mL STOCK SOLN plus 5 mL HNO_3/1 Liter — Time On _____ Temp (°C) _____

SOLUTION II - 0.1 mg/L Hg — Time _____ Temp (°C) _____

10.0 mL SOLN I plus 5 mL HNO_3/1 Liter — Time _____ Temp (°C) _____

SOLUTION III - 0.01 mg/L Hg — Time _____ Temp (°C) _____

10.0 mL SOLN II plus 0.5 mL HNO_3/100 mL — Time _____ Temp (°C) _____

Time Off _____ Temp (°C) _____

Final Dilution	Final Conc.	Peak Height (T%)	Absorbance
0.0 mL	0.0000 mg/L	_____	_____
2.0 mL SOLN III/100 mL	0.002 mg/L	_____	_____
5.0 mL SOLN III/100 mL	0.0005 mg/L	_____	_____
10.0 mL SOLN III/100 mL	0.0010 mg/L	_____	_____
3.0 mL SOLN II/100 mL	0.0030 mg/L	_____	_____
5.0 mL SOLN II/100 mL	0.0050 mg/L	_____	_____
7.0 mL SOLN II/100 mL	0.0070 mg/L	_____	_____
10.0 mL SOLN II/100 mL	0.0100 mg/L	_____	_____
0.0 mL	0.0000 mg/L	_____	_____

Correlation Coefficient (r): _____

CALCULATIONS:

$$Absorbance = 2 - \log (\%T)$$

$$mg/L\ Hg = (Curve\ Reading)\left(\frac{100\ mL}{Sample\ Aliquot}\right)(Dilutions)$$

FIGURE 4

WORKSHEET
October 27, 1992
Mercury

Analyte: Mercury, Total (Hg) BATCH 30089

Sample	Type	Client	Date Sampled	Date Received	Date Due		Prep	Anls	Sample Description
214543	DUP		21-SEP-92	08-OCT-92		00		AHGSR-	PCTU / AS REC'D
214543	MS		21-SEP-92	08-OCT-92		00		AHGSR-	PCTU / AS REC'D
214543	ORIG		21-SEP-92	08-OCT-92		00		AHGSR-	PCTU / AS REC'D
214546	ORIG		21-SEP-92	08-OCT-92		00		AHGSR-	PCH / AS REC'D
215158	LCSR		20-OCT-92	20-OCT-92		00		AHGS	Lab Control Sample
215159	BLNK		20-OCT-92	20-OCT-92		00		AHGS	Method Blank

SAMPLE INSTRUCTIONS

P214543 LAB TRACKED
P214543 TYPE C
P214546 LAB TRACKED
P214546 TYPE C

Ref.	Analysis Date	Instrument	Anlst	Start Time	Run File	Comments
1	10/26/92	MAS 508	2005X	1030	hg921026	Print file = hg1026
2						
3						
4						
5						

Sample	Type	Ref	Diln.	Cup	Result	Unit	Book	Page	Range	RPD	MSR % Rec	IV/SA	Reviewed
214543	DUP	1	1	L	1.18	mg/kg	P140-92	118		7.02			
214543	MS	1	1	M	2.09						104	0.949	
214543	ORIG	1	1	K	1.1								
214546	ORIG	1	1	W	<0.1								
215158	LCSR	1	1	J	10.6						112	9.5	
215159	BLNK	1	1	I	<0.1								

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CORPORATION

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LABORATORY METHOD

TOTAL CYANIDE

METHOD ID: CRA/SN-CN
REVISION: 0
EFFECTIVE DATE: 04/13/94

APPROVALS:

See page 1 of the method.

TOTAL CYANIDE

1.0 SCOPE AND APPLICATION

This method is applicable to the determination of total cyanide in drinking, surface ground and saline waters, domestic and industrial wastes, and soil/sediment or waste.

2.0 SUMMARY OF METHOD

After acidification, the cyanide is released from complexed cyanide by reflux-distillation and is collected as hydrocyanic acid (HCN) in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

In the colorimetric procedure, the cyanide is converted to cyanogen chloride (CNCl) by reaction with chloramine-T at low pH. Color is developed upon addition of pyridine-barbituric acid reagent. Absorbance is measured at 578 nm by a spectrophotometer. A standard curve is developed using known concentrations of cyanide in solution. Sample concentrations are measured from the standard curve.

3.0 PROCEDURE

3.1 STANDARDIZATION OF SOLUTIONS

3.1.1 Prepare the potassium cyanide stock, silver nitrate standard and chloride standard solutions as directed in Sections 9.2-9.4.

3.1.2 Determine the normality of the silver nitrate standard after preparation as follows:

a. Attach the glass and silver-silver chloride electrodes to a mV meter with an expanded scale.

b. Pipet 10.0 mL of 0.01 N chloride standard (KCl) into a 250-mL beaker and dilute to 100 mL with reagent water.

Approvals:

Charles A Kiede	4/12/94	G. L. Colbert	4-12-94	Lisa Manning	4/12/94
Technical Operations Manager	Date	Group Leader	Date	Quality Assurance Director	Date

c. Add 2.0 mL concentrated HNO_3 and a small stir bar.

d. Immerse the electrodes slowly and record the initial mV reading.

Note: Maintain an even stirring rate. Avoid large air bubbles under the electrodes by adjusting the stir rate or re-immersing the electrodes.

e. Add 0.01 N $AgNO_3$ titrant in small increments using a buret. Record the mV readout after each increment. See Figure 1 for a titration example.

Note: Avoid stopping the titration too early or too few points will be available to draw the line beyond the end-point.

f. Plot mV vs. mL $AgNO_3$ to determine the endpoint of the titration. The end-point is the mid-point of the straight line connecting the two parallel lines as indicated in Figure 2.

g. Repeat steps 3.1.2b-e until the $AgNO_3$ titers agree within 1 mL and the mV readings within $\pm$ 2 units.

h. Calculate the normality (N) of the $AgNO_3$ standard using the following equation:

$$N = \frac{0.01\ N\ KCl \times 10\ mL\ KCl}{mL\ AgNO_3\ at\ endpoint}$$

3.1.3 Standardize the potassium cyanide stock monthly as follows:

a. Transfer 50 mL of 250 mg/L KCN stock to a flask and dilute to 100 mL with 0.04 N NaOH.

b. Add 0.5 mL rhodamine indicator.

c. Titrate with standard $AgNO_3$ using a microburet to the first color change from yellow to salmon pink. Record the buret reading.

d. Repeat steps 3.1.3a-c until the titers agree within 0.5 mL.

e. Titrate a blank of 0.04 N NaOH following steps 3.1.3a-d.

f. Calculate the cyanide concentration of the KCN stock solution using the following equation:

$$mg/L\ CN = \frac{(A-B) \times N\ AgNO_3 \times 0.052}{50\ mL\ KCN\ stock} \times 10^6$$

where A = mL $AgNO_3$ needed to titrate standard
B = mL $AgNO_3$ needed to titrate blank
N $AgNO_3$ was calculated in step 3.1.2.h

g. Calculate the proper aliquot of KCN stock required to prepare a liter of 2.5 mg/L CN as follows:

$$X = \frac{2.5 \text{ mg/L CN}}{\text{mg/L CN stock conc.}} \times 1000 \text{ mL}$$

where (mg/L CN stock concentration) was calculated in 3.1.3.f.

3.1.4 Complete the standardization process as follows:

a. Prepare the working standards as directed in Section 9.2.

b. Distill and measure absorbance in the working standards as described in Sections 3.3 and 3.4.

c. Prepare standard curves, as described in Figures 3 and 4, of mg/L CN vs. net absorbance per cell size (i.e., 1 and 5 cm cells).

3.2 SAMPLE PREPARATION

3.2.1 Analyze samples preserved with NaOH solution to pH >12 and refrigerated at 4°C. Check the sampling (i.e., collection) date and analyze the samples within 14 days of sampling.

Note: Test all samples for sulfide and chlorine interference and pretreat as necessary. Test and pretreat for the other interferences as necessary. Consult with the Group Leader, if required, to determine the necessity of additional interference testing.

3.2.2 Test and pretreat for sulfide as follows:

a. Moisten a strip of lead acetate test paper with acetic acid (1:9, v/v). Place a drop of sample on the test paper and check for darkening to indicate the presence of sulfide.

b. If sulfide is present, add lead nitrate solution or lead carbonate powder as follows:

- If lead nitrate solution is used, check and adjust the pH to 12 (approx.) before proceeding. Add the lead nitrate solution dropwise to the sample and mix thoroughly.

- Lead carbonate powder is preferred only when significant

quantities of sulfides are present and the addition of sufficient lead nitrate solution to remove it would depress the sample pH.

Avoid adding excess lead carbonate because cyanide could be lost by adherence to the powder.

c. Repeat steps 3.2.2a-b as necessary until lead sulfide is no longer detected.

d. Immediately filter the sample through dry filter paper (0.45 μ) into a vacuum flask.

e. Test a small portion of the filtrate for sulfide as described in step 3.2.2a before proceeding with chlorine testing. If sulfide is present, repeat steps b through e.

3.2.3 Test and pretreat for chlorine as follows:

a. Moisten a strip of potassium iodide-starch test paper with acetic acid (1:9, v/v). Place a drop of sample on the paper and check for bluish darkening to indicate chlorine.

b. Add 0.1 g of sodium arsenite per liter of sample if chlorine is present. Retest as described in step 3.2.3a.

c. Repeat the sodium arsenite addition as necessary until retesting is negative for chlorine.

d. Use a suitable aliquot from the pretreated sample for the distillation described in Section 3.3.

3.2.4 Pretreat the samples if necessary for fatty acids or oils as follows:

a. Acidify the sample with acetic acid (1:9, v/v) to pH 6-7.

Note: Perform this step in a hood due to the possible evolution of toxic HCN gas.

b. Extract the sample in a separatory funnel using iso-octane, hexane or chloroform, in order of preference, as follows:

- Transfer the sample aliquot measured in a graduated cylinder to a separatory funnel and stopper it. Record the volume in the data logbook.

- Add a solvent volume equal to approximately 20% of the sample volume, measured in a graduated cylinder, to the separatory

funnel.

- Seal the separatory funnel. Invert several times and vent the funnel into the hood by opening the stopcock.

  Close the stopcock. Continue to shake and vent for approximately 30 seconds.

- Allow the layers to separate and discard the solvent layer.

c. Immediately, adjust the sample pH to >12 with NaOH solution.

3.2.5 Pretreat the samples if necessary for nitrite as follows:

a. Transfer a small amount of sample to a beaker and adjust the pH to approximately 7. Add approximately 1 mL of 1-naphthylethylenediamine reagent and check for a pink reaction to indicate nitrite.

b. Add 2 g of sulfamic acid per 500 mL of sample if nitrite is present. Add the sulfamic acid before the addition of H_2SO_4 as described in step 3.3.8.

3.2.6 Pretreat the samples if necessary for aldehydes as follows:

a. Transfer a small aliquot of sample to a beaker and adjust the pH <8 using H_2SO_4.

b. Test the sample aliquot for aldehydes as follows:

- Place one drop each of sample and reagent water into separate wells of a white spot plate.

- Add one drop each of MBTH indicator and $FeCl_3$ oxidizing solution to each well. Mix with a stirring rod.

c. Check for color development after 10 minutes. A color change from a fruit-green-yellow to a deeper green or blue-green indicates a positive reaction.

d. Add 2 mL of 3.5% ethylenediamine solution per 100 mL of sample if aldhydes are present.

3.3 DISTILLATION

Note: Refer to Figure 5 to assemble the distillation apparatus. Refer to Figure 6 for the distillation/analytical sequence.

3.3.1 Add 100 mL of 0.1 N NaOH and 1 mL (approx.) of 5% $Pb(NO_3)_2$ in the Fisher-Milligan gas washing bottle. Insert the bubble tube and tighten the cap securely to prevent air bubbles.

3.3.2 Attach the gas washing bottle to the vacuum and the extension tube to the bottle. Check that the vacuum does not draw adsorption solution out of the collecting bottle.

3.3.3 Determine the sample aliquot as follows:

a. Place a small amount of sample in a beaker and add the reagents for color development described in steps 3.4.2 and 3.4.3.

Note: Exact timing for color development is not necessary at this point.

b. Determine a sample aliquot, up to a maximum of 500 mL or 5 g, that contains $\leq$ 5 mg of cyanide (i.e., 10 mg/L). Dilute concentrated sample aliquots with 0.04 N NaOH.

3.3.4 Add the sample aliquot and boiling beads and chips to the 1000 mL round-bottom flask. Add reagent water as necessary to bring the final volume to 500 mL.

3.3.5 Place the air inlet tube in the flask and connect the sidearm to the condenser.

3.3.6 Turn on the vacuum and adjust the airflow entering the boiling flask to approximately one bubble per second.

Note: Turn on the vacuum at the source and at the stopcock. Regulate the vacuum rate by adjustment of the stopcock.

Check that the bubbles pass through each coil in the gas washing bottle.

3.3.7 Add 20 mL of $MgCl_2$ solution through the air inlet tube.

3.3.8 Rinse the air inlet tube with reagent water and allow the air flow to mix the contents of the flask for approximately five minutes.

Note: Add sulfamic acid, if necessary, as described in step 3.2.5.b to remove nitrites at this time.

3.3.9 Add 50 mL of H_2SO_4 (1:1, v/v) through the air inlet tube. Rinse the tube with reagent water and mix well.

3.3.10 Turn on the condenser cooling water. Heat the solution to boiling while preventing solution backflow into the air inlet tube by adjusting the stopcock.

Adjust the air flow to the proper rate described in step 3.3.6 before proceeding to more samples.

Note: Avoid starting too many samples at once because each sample will require special attention when the boiling point is reached.

Watch the sample closely as it approaches the boiling point to prevent solution backflow into the air inlet tube. Open the stopcock to force the liquid down the tube as necessary. Avoid opening the stopcock for long periods because HCN will be lost to the atmosphere.

3.3.11 Reflux for 1 hour.

3.3.12 Turn off the heat but maintain air flow for 15 minutes after the distillation period.

3.3.13 Quantitatively transfer the absorption solution into a 250-mL stoppered graduated cylinder. Rinse the flask with several small quantities of reagent water to complete the transfer. Dilute to volume with reagent water, stopper the cylinder and invert several times to mix well.

Note: Filter distillates containing a brown or black precipitate of excess sulfide through a 0.45 μ filter after diluting to volume. Prepare two separate aliquots, differing by at least a factor of 2, for color development.

Consult with the Group Leader, if required, to determine if the results of these aliquots indicate the sample needs redistilled.

3.4 COLORIMETRIC MEASUREMENT

Note: Calibrate and use the spectrophotometer according to the manufacturer's guidelines.

Prepare a maximum of 6 samples at one time for color development.

3.4.1 Transfer 40 mL of distillate, or an aliquot diluted to 40 mL with 0.04 N NaOH, into a 50-mL stoppered graduated cylinder.

3.4.2 Add 1.0 mL of chloramine-T solution and 1.0 mL of acetate buffer, stopper the cylinder and invert 2-3 times to mix well. Allow to stand undisturbed for <u>exactly</u> 2 minutes.

Note: Chloramine-T is volatile. To prepare multiple samples, add the reagents, mix and begin timing on one sample at a time.

3.4.3 Add 5.0 mL of pyridine-barbituric acid reagent and dilute to volume with reagent water. Mix thoroughly and allow to stand undisturbed 8 minutes.

3.4.4 Zero the spectrophotometer with reagent water. Measure the absorbance (A) of the samples at 578 nm using a 1 or 5 cm cell.

Note: Observe proper timing - all samples must be measured within 15 minutes after addition of the pyridine-barbituric reagent.

3.4.5 Prepare 40 mL of 0.04 N NaOH as described in steps 3.4.2-3.4.4 for use as a blank.

3.5 CALCULATIONS

3.5.1 Water sample calculations:

$$\text{mg/L CN} = \text{CF} \times \text{Net Abs.} \times \frac{250\ \text{mL}}{\text{SA(mL)}} \times \frac{50\ \text{mL}}{\text{CA(mL)}} \times \text{Dilutions}$$

where CF = Curve factor
SA = Sample aliquot in mL
CA = Color aliquot in mL

3.5.2 Solid sample calculations:

$$\text{mg/kg CN} = \text{CF} \times \text{Net Abs.} \times \frac{250\ \text{mL}}{\text{SA (g)}} \times \frac{50\ \text{mL}}{\text{CA(mL)}} \times \text{Dil'ns}$$

where CF = Curve factor
SA = Sample aliquot in grams (wet weight)
CA = Color aliquot in mL

4.0 DATA COLLECTION

4.1 Document all data in a bound lab notebook for each set of distillations and measurements performed. Entries must be made at the time of distillation and measurement. Examples for standard curve data collection are shown in Figures 3 and 4. An example data logbook entry is shown in Figure 7.

Data collection for samples should include the following:

- analytical method and preparation method code and brief description.

- date and time distillation started and completed, and analyst(s) signature(s) and identification number(s).
- date and time colorimetric measurement started and completed, and analyst(s) signature(s) and identification number(s).
- data values for each sample.
- NUS laboratory sample number and aliquot. Identify any lab quality control samples (method blanks, matrix spike (MS)/duplicates, LCSs).
- spikes added, to include the spiking solution identification number and the volume of spike added.

4.2 Forward the following to data management from each analytical run:

- preparation raw data, including standards/spiking solutions preparation pages.
- analytical raw data, including logbook page(s) with all samples and associated quality control samples.
- standard curve data.
- description of problems encountered and actions taken during sample preparation and analysis on corrective action records.
- any instrument maintenance documented in the instrument maintenance log.

5.0 QUALITY CONTROL

5.1 METHOD BLANKS

Prepare and analyze a method blank (i.e., 0.04 N NaOH) with each batch of samples distilled.

If more than 20 samples are included in a batch, prepare an additional method blank.

Note: In such cases, both blanks will be applicable to all samples in the batch for the purpose of quality control evaluation.

The absolute value of the method blank must be < the reporting limit. If it is not, the samples associated with the nonconforming blank that also contain total cyanide at levels from the reporting limit to 10 times the level in the blank must be redistilled.

5.2 CALIBRATION

The calibration standard series described on Figures 3 and 4 must be run annually at a minimum. The curve is run in triplicate for both 1 and 5 cm cells. An average factor is calculated. Run laboratory control standards (LCSs) to check curve validity as described in Section 5.3.

If this initial LCS does not pass the criteria in Table 1 take corrective action that may include recalibration.

5.3 DAILY STANDARD

Prepare a daily standard, an independently traceable standard distilled with the samples, at the start and end of the run and for every batch of up to 10 samples. The recovery limits are 83.8 - 119%. If the limits are not met, terminate analysis and troubleshoot the system. If the problem can not be located, reanalyze the entire batch; otherwise, reanalyze the affected samples.

These limits are statistically based and are updated semi-annually; they are subject to change.

5.4 LABORATORY CONTROL SAMPLES (LCS)

Run a solid reference material for each batch of up to 20 solid samples for total cyanide. The LCS control limits are 79.9 - 124%. If an LCS fails, redistill and reanalyze all associated samples in the batch.

These limits are statistically based and are updated semi-annually; they are subject to change.

5.5 REPORTING LIMIT (RL) STANDARD

Analyze a standard at the concentration of the reporting limit immediately after the first daily standard of each analysis sequence. The RL must recover $\geq$50%. If it does not, terminate analysis and troubleshoot the system.

5.6 MATRIX SPIKES AND DUPLICATES (MS/DUP)

Measure a matrix spike and duplicate for every 1 in 10 samples daily as follows:

- The MS consists of an aliquot of sample and an aliquot of a standard solution.

  Spike recoveries outside 75.0 to 125% are qualified provided daily standard recoveries are acceptable.

- The duplicate analysis consists of a second aliquot of a sample processed in

the same manner as the original aliquot.

Limits for precision are RPD ≤27.1%, range <2DL (waters) and RPD ≤17.2%, range <4DL (soils). Reanalyze the duplicate sample when precision is unacceptable. Spotcheck 25% of the positive results if it remains nonconforming. Rerun all samples and report recheck results if spotchecks do not duplicate original results.

These limits are statistically based and are updated semi-annually; they are subject to change.

5.7 METHOD DETECTION LIMIT STUDIES

A method detection limit (MDL) study for water analysis is performed annually. Statistically-based MDLs must be ≤ reporting limits for the method.

6.0 INTERFERENCES

6.1 Solvents, reagents, glassware, and other sample processing hardware may be sources of contamination and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Use of specific grades of reagents is required.

6.2 Sulfides slowly convert cyanide to thiocyanate (SCN). Some sulfur compounds may decompose during the acid digestion/distillation to release H_2S gas into the adsorption solution causing discoloration.

6.3 Oxidizing agents such as chlorine destroy cyanide during analysis. Addition of sodium arsenite to samples containing oxidizers is recommended.

6.4 Fatty acids that distill into the adsorption solution cause turbidity. Fatty acids, if present, are removed by solvent extraction at low pH prior to distillation.

6.5 Aldehydes combine with cyanide to form cyanohydrins that convert to the corresponding carboxylic acids resulting in little or no generation of HCN. Aldehyde interference may be minimized by the addition of ethylene diamine to the sample.

6.6 This method does not distinguish between cyanide ions and metallocyanide compounds and complexes. Cyanates and cyanogen halides are not detected. The cyanide in cyano-complexes of cobalt, gold and platinum are not completely determined. Only a few organo-cyanide complexes are partially recovered.

7.0 SAFETY PRECAUTIONS

7.1 Cyanide is acutely toxic by dermal, inhalation or oral routes of entry. Use requisite safety equipment to avoid contact during sample processing and disposal.

7.1.1 Wear a lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with acids, bases, organic solvents and possible toxicants used as reagents or contained in the samples for analysis.

Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

7.1.2 Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

7.1.3 Manipulate highly concentrated standards or samples during acidification in a closed system or under an operating fume hood.

7.2 Dispose of cyanide-containing samples and reagents according to established laboratory waste disposal guidelines.

7.3 Handle and store all reagents in accordance with the precautions listed on the Material Safety Data Sheets (MSDS).

7.3.1 Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.

7.3.2 Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions and expiration data.

7.3.3 Label all flasks, vials, etc., with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

7.4 Avoid breathing solvent and standard solution vapors.

If overexposure to vapors should occur, seek fresh air and immediate medical attention.

7.5 When preparing dilute solutions of concentrated acids, ALWAYS ADD ACID to WATER.

7.6 Handle all glass equipment with care, particularly during assembly and

disassembly.

8.0 APPARATUS AND MATERIALS

8.1 Distillation apparatus: Refer to Figure 5 for assembly information.

8.1.1 **Round-bottom flask:** 1000-mL with T/s joint.

8.1.2 **Condenser:** Allihn water-cooled condenser.

8.1.3 **Air inlet tube:** Tube with T/s joint.

8.1.4 **Adaptors.**

8.1.5 **Gas washer:** Fisher-Milligan spiral-type washer.

8.1.6 **Extension tubes.**

8.1.7 **Rubber tubing.**

8.2 Graduated cylinders: 250- and 50-mL stoppered, glass cylinders.

8.3 Heaters: Mantle-type.

8.4 Timer: Accurate to 1 minute.

8.5 Microburet: 10-mL glass buret.

8.6 Flasks: 500-mL Erlenmyer flasks.

8.7 Spectrophotometer: Use at 578 nm and provide a light path of 50 mm or longer.

9.0 REAGENTS

9.1 Reagent water: Deionized water.

9.2 Potassium Cyanide Solutions:

9.2.1 **Potassium Cyanide Stock Solution (nominally 250 mg/L CN)** -Dissolve 0.6258 g of potassium cyanide (KCN) in 40 ml of 1 N NaOH solution in a 1-L volumetric flask. Dilute to volume with reagent water and mix thoroughly. Standardize with standard silver nitrate solution monthly as described in Section 3.1.

Store at 4°C in a dark bottle. Prepare a fresh solution each time standard curves are done and when recovery data indicates

deterioration.

9.2.2 **Potassium Cyanide Solution I (nominally 2.5 mg/L CN)** - Dilute 10.0 mL of KCN stock solution and 36 ml of 1 N NaOH solution to volume with reagent water in a 1-L volumetric flask. Mix thoroughly.

Prepare fresh daily.

9.2.3 **Potassium Cyanide Solution II (nominally 0.25 mg/L CN)** - Dilute 20.0 ml of KCN solution I and 7 ml of 1 N NaOH solution to volume in a 200-mL volumetric flask with reagent water. Mix thoroughly.

Prepare fresh daily.

9.3 Silver Nitrate Standard Solution (0.01 N): Dissolve 1.6987 g $AgNO_3$ in reagent water and dilute to volume in a 1-L volumetric flask. Mix thoroughly. Determine the normality as described in Section 3.1.

9.4 Chloride Standard Solution (0.01 N): Dissolve 0.7456 g of KCl (NIST grade - dried at 105°C for 1 hour and stored desiccated) in reagent water and dilute to volume in a 1-L volumetric flask. Mix thoroughly.

9.5 Sodium Hydroxide Solutions:

9.5.1 **Sodium Hydroxide Solution (10 N)** - Dissolve 400 g of NaOH pellets in reagent water in a 1-L flask. Dilute to volume and mix thoroughly. Alternatively, purchase commercially prepared solution.

9.5.2 **Sodium Hydroxide Solution (1 N)** - Dilute 100 mL of 10 N NaOH solution to volume in a 1-L flask. Mix thoroughly. Alternatively, purchase commercially prepared solution.

9.5.3 **Sodium Hydroxide Solution (0.1 N)** - Dilute 10 ml of 10 N NaOH solution to volume in a 1-L flask. Mix thoroughly.

9.5.4 **Sodium Hydroxide Solution (0.04 N)** - Dilute 4.0 mL of 10 N NaOH solution to volume in a 1-L flask. Mix thoroughly.

9.6 Nitric Acid: C.P. grade, concentrated.

9.7 Rhodamine Indicator Solution: Dissolve 0.02 g of p-dimethylamino-benzylidene in 100 mL of acetone in a volumetric flask. Mix thoroughly.

Store at 4°C in a dark bottle.

9.8 Sodium Acetate Buffer: Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of reagent water in a beaker. Add glacial acetic

acid to pH 4.5 (approx. 500 mL). Mix thoroughly.

9.9 Chloramine-T (1%): Dissolve 1.0000 g of the white-colored, water-soluble grade powder chloramine-T in 100 mL of reagent water in a volumetric flask. Mix thoroughly.

Store under refrigeration in a dark bottle. Return the solution immediately to the refrigerator when not in use. Prepare fresh weekly.

9.10 Magnesium Chloride Solution: Dissolve 510 g of magnesium chloride ($MgCL_2 \bullet 6H_2O$) in reagent water and dilute to 1 liter. Mix thoroughly.

9.11 Lead Nitrate Solution: Dissolve 50 g of $Pg(NO_3)_2$ in 1 liter of reagent water. Mix thoroughly. Lead acetate [$Pb(OAC_2)$] may be substituted.

9.12 Sulfuric Acid (1:1, v/v): **Slowly** add 1 volume of concentrated sulfuric acid to 1 volume of reagent water. Stir and cool the solution during the addition.

9.13 Pyridine-Barbituric Acid Reagent: **Prepare this solution under a hood.** Add 60 g of barbituric acid and just enough reagent water to wash the sides of a 1-L flask and wet the barbituric acid. Add 300 mL of pyridine and mix. Add 60 mL of concentrated hydrochloric acid all at once and additional reagent water to dissolve the barbituric acid. Mix thoroughly and cool to room temperature. Dilute to volume with reagent water and mix.

Store at 4°C in a dark bottle. Prepare fresh every six months.

9.14 Acetic Acid (1:9, v/v): Mix 1 volume of glacial acetic acid with 9 volumes of water.

9.15 Ethylene Diamine (3.5%): Dilute 3.5 ml of pharmaceutical grade anhydrous $NH_2CH_2NH_2$ to volume with reagent water in a 100-ml flask. Mix thoroughly.

9.16 Ferric Chloride Oxidizing Solution: Dissolve 1.6 g sulfamic acid and 1 g $FeCL_3 \bullet 6H_2O$ in 10 ml of reagent water. Mix thoroughly.

9.17 MBTH Indicator Solution: Dissolve 0.05 g 3-methyl,2-benzothiazolone hydrochloride in 100 ml of reagent water. Mix thoroughly. Filter if turbid.

9.18 Sulfamic Acid: Powder.

9.19 Sodium Arsenite: Powder.

9.20 Naphthylethylenediamine Reagent: Add 105 mL concentrated HCl, 5.0 g sulfanilamide and 0.5 g N-(1-naphthyl)ethylenediamine dihydrochloride to 250 mL of reagent water. Stir to dissolve. Add 136 g sodium acetate ($CH_3COONa \bullet 3H_2O$) and stir to dissolve. Dilute to 500 mL with reagent water.

Store in the dark. Prepare fresh monthly.

9.21 Solid Reference Material: Commercially prepared standard reference material used as a LCS when running solid samples.

10.0 REFERENCES

10.1 "Annual Book of ASTM Standards," Volume 11.02, 1987, Method D-2036.

10.2 U.S. EPA 600/4-79-020, "Methods for Chemical Analysis of Water and Wastes," March 1979; Method 335.2.

10.3 "Standard Methods for the Examination of Water and Wastewater," 17th Edition, 1989, Method 4500-CN A-E.

FIGURE 1

STANDARDIZATION OF $AgNO_3$ POTENTIOMETRIC TITRATION

Standard KCl Solution (0.01 N)
0.7456g NBS Grade KCl/1000 ml Lot # KCl _____

Standard $AgNO_3$ Solution (0.01 N)
1.698g/1000 ml

Manufacturer/Lot # $AgNO_3$ _____

Titrate 10.0 mL of 0.01N KCl with 0.01N $AgNO_3$. Measure the potential of the KCl solution at the intervals specified below.

ml $AgNO_3$	mv	instrument
0.0		
1.0		
2.0		
3.0		
4.0		
5.0		
6.0		
7.0		
8.0		
8.5		
9.0		
9.2		
9.4		
9.6		
9.7		
9.8		
9.9		
10.0		
10.1		
10.2		
10.3		
10.4		
10.5		
10.6		
10.8		
11.0		
12.0		
13.0		
14.0		
15.0		

Analyst _____ Date _____

FIGURE 2

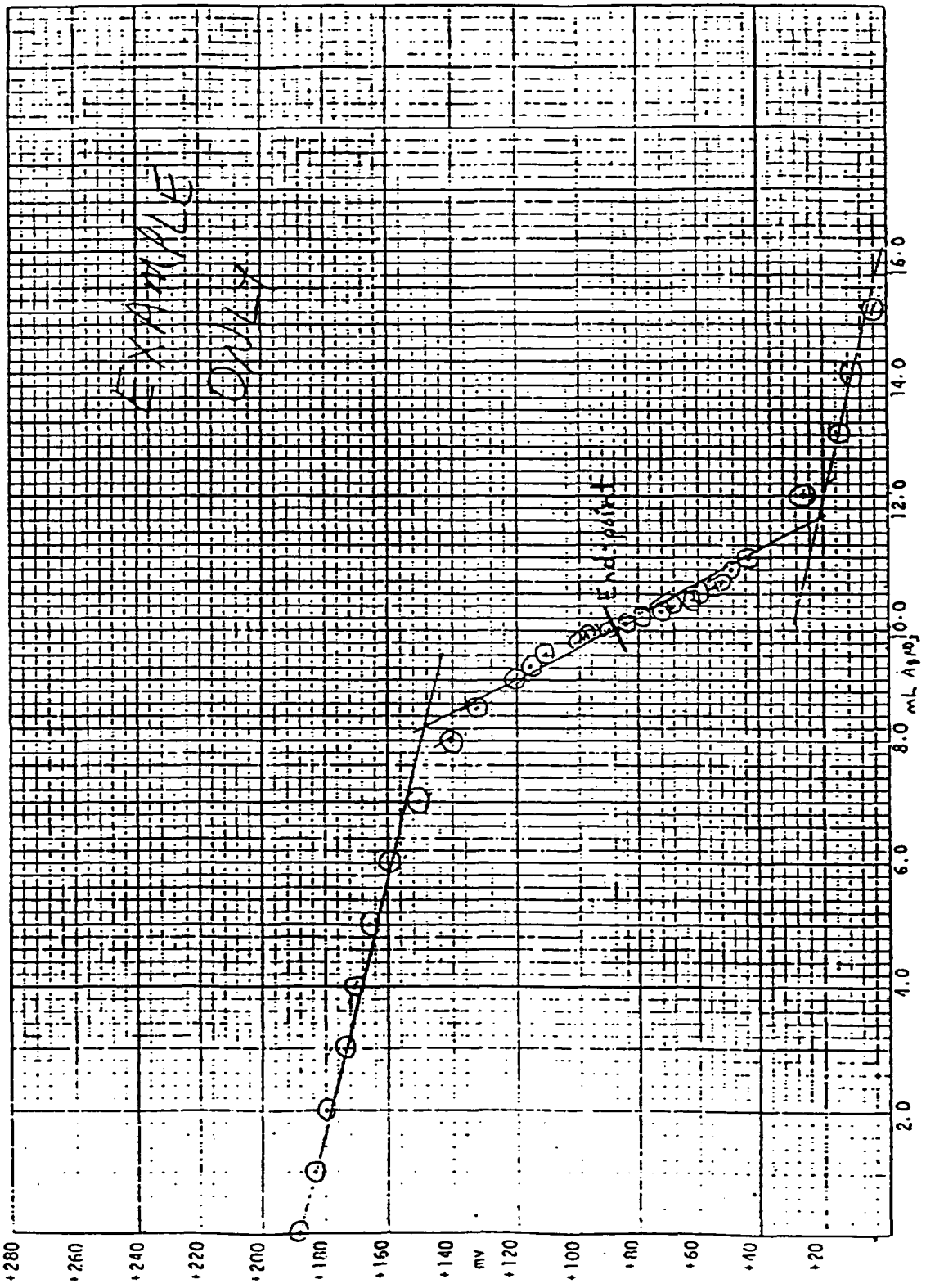

+280
+260
+240
+220
+200
+180
+160
+140
+120
+100
+80
+60
+40
+20
mv
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
mL AgNO3
End point
DIETZGEN CORPORATION
NO. 340-10 DIETZGEN GRAPH PAPER
10 X 10 PER INCH

FIGURE 3

W270
TOTAL CYANIDE
Standard Curve

Date:_____
Analyst:_____
Instrument:_____
Wavelenght: 578 nm
Cell Width: 5 cm

Stock Standard Solution: 250 mg/L CN
0.6258 g KCN + 40 mL of 1N NaOH/1000 mL
Manufacturer/Lot#_____

Solution I: 2.5 mg/L CN
10.0 mL Stock + 36 mL of 1N NaOH/1000 mL

Solution II: 0.25 mg/L CN
20.0 mL Soln I + 7 mL of 1N NaOH/200 mL

Working Standards mL Soln II/250 mL	Color Aliquot (mL)	Concentration (mg/L)	Absorbance at 578 nm	Net Abs.	Concentration Net Abs.
0.0	25	0.000	_____	____	_____
10.0	25	0.005	_____	____	_____
20.0	25	0.010	_____	____	_____
30.0	25	0.015	_____	____	_____
40.0	25	0.020	_____	____	_____
50.0	25	0.025	_____	____	_____

FACTOR* = Average Conc./Net Abs. = [ ]

mg/L CN = Factor X Net Abs. X $\frac{250\ mL}{\text{Sample Aliq. (mL)}}$ X $\frac{50\ mL}{\text{Color Aliq. (mL)}}$ X dilutions

* Color Development Conditions
1.0 mL 1% Chloramine - T
1.0 mL Sodium Acetate Buffer
5.0 mL Pyridine Barbituric Acid

Approved by:_____
Date:_____

FIGURE 4

W270
TOTAL CYANIDE
Standard Curve

Date:_____
Analyst:_____
Instrument:_____
Wavelength: 578 nm
Cell Width: 1 cm

Stock Standard Solution: 250 mg/L CN
0.6258 g KCN + 40 mL of 1N NaOH/1000 mL
Manufacturer/Lot#_____

Standard Solution I: 2.5 mg/L CN
10.0 mL Stock + 36 mL of 1N NaOH/1000 mL

Working Standards mL Soln I/250mL	Color Aliquot (mL)	Concentration (mg/L)	Absorbance at 578 nm	Net Abs.	Concentration Net Abs.
0.0	25	0.000			
5.0	25	0.025			
10.0	25	0.050			
15.0	25	0.075			
20.0	25	0.100			
25.0	25	0.125			
30.0	25	0.150			

FACTOR* = Average Conc./Net Abs. = [ ]

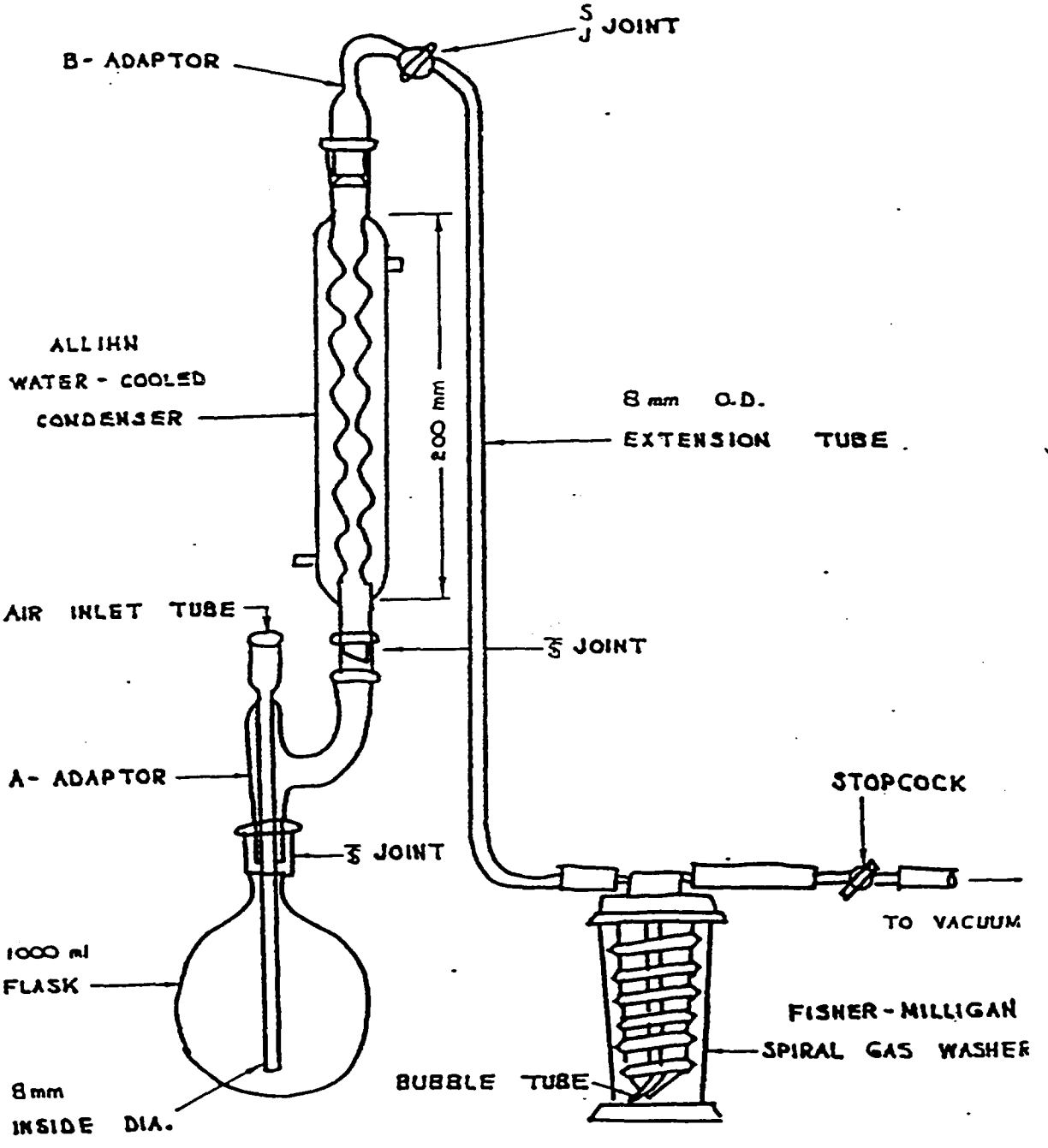
$$mg/L\ CN = Factor \times Net\ Abs. \times \frac{250\ mL}{Sample\ Aliq.\ (mL)} \times \frac{50\ mL}{Color\ Aliq.\ (mL)} \times dilutions$$

*Color Development Conditions
1.0 mL 1% Chloramine - T
1.0 mL Sodium Acetate Buffer
5.0 mL Pyridine Barbituric Acid

Approved by:_____
Date:_____

CTP 4-14-94

FIGURE 5



CYANIDE DISTILLATION APPARATUS.

FIGURE 6

Total Cyanide Determinations

Distillation/Analytical Sequence

Method Blank 1
Detection Limit Standard*
Laboratory Control Standard (Curve Check 1)
Sample 1
Sample 1 - duplicate
Sample 1 - matrix spike
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7
Sample 8
Sample 9
Sample 10
Laboratory Control Standard (Curve Check 2)
Sample 11
Sample 11 - duplicate
Sample 11 - matrix spike
Sample 12
Sample 13
Sample 14
Sample 15
Sample 16
Sample 17
Sample 18
Sample 19
Sample 20
Method Blank 2
Laboratory Control Standard (Curve Check 3)
↓
Repeat analytical sequence as necessary to analyze all samples.
↓
Laboratory Control Standard (Curve Check n)

* The absorbance of the detection limit standard must be discernable above that of the method blank for analysis to continue.

FIGURE 7

TITLE EXAMPLE ONLY

PROJECT NO.

BOOK NO.: P192-92

107

TEST Total CN	INSTRUMENT SACC 21-3	BATCH See Below	
TEST CODE I270	FACTORS 5cm 0.0657 / 0.005	ANALYST # JA/P0070	* Init STD (#8, 1-27-92-137)
AU I145C	1cm 0.242 / 0.121	DATE start 6/22/92 end 6/23/92	Det Limit (#9, 1-27-92-137)
PW I05 4TZ	CURVE DATE 12/14/91	TIME start 0800 finish 1130	
STANDARD REFERENCE *	TITER NORMALITY N/A		

Total CN Batch # 10887

Sample #	Client	D Alk (mL)	Dil (mL)	C Alk (mL)	Cell Size	Abs	Net Abs	Init Result	Result mg/L
Dist Blank	P204498	500	–	40	5cm	0.046	0.023	0.000792	<0.005
Detect Limit (10 mL)		250	–	↓	↓	0.035	0.012	0.000825	0.00825
LCS	P204497	10 mL of 25 mg/L	–			0.068	0.045	0.0774825	2.42 (96.9%)
P203067	AAC, Inc.	250	–			0.039	0.016	0.001102	<0.005
P203068	↓	↓	–			0.055	0.032	0.002204	<0.005
P203069			–			0.041	0.018	0.0012397	<0.005
P203392		↓	–			0.040	0.017	0.0011708	<0.005
P203392D		100	–			0.035	0.012	0.0020662	<0.0125
P203392 MS+	↓	100 mL	–			0.075	0.052	0.0089537	0.255
#1-127-92+100		+ 10 mL of 25 mg/L	–	↓	↓				MSR = 102.13%
LCS		10 mL of 25 mg/L	–	40	5cm	0.48	0.045	0.0774825	2.42 (96.9%)

SCIENTIFIC BINDERY PRODUCTS CHICAGO

SIGNATURE Jane Analyst DATE 6/22/92

DISCLOSED TO AND UNDERSTOOD BY Frank Smith DATE 6-23-92 WITNESS DATE

pace
INCORPORATED
THE ASSURANCE OF QUALITY

STANDARD OPERATING PROCEDURE

Sample Receipt And Check-In

SOP NUMBER	MN-C-702-F
AUTHOR	Sue Lautt
EFFECTIVE DATE	October 5, 1993
SUPERSEDES	MN-C-702-E

APPROVAL

Sample Receiving Supervisor — Date: 10/06/93

Manager, Marketing & Client Services — Date: 10/06/93

Quality Assurance Officer — Date: 10/6/93

TABLE OF CONTENTS

I. PURPOSE

A. The purpose of this Standard Operating Procedure (SOP) is to establish a uniform and efficient system for the receipt of samples into the laboratory.

II. SCOPE

A. The policies and procedures contained in this SOP are applicable to all Sample Custodians and Check-In personnel of PACE, Incorporated.

III. RESPONSIBILITIES

A. QUALITY ASSURANCE OFFICER (QAO)

1. The QAO is responsible for monitoring implementation and adherence to this SOP.

2. The QAO will provide copies of this SOP to the Sample Custodians, Receiving Technicians, and other appropriate personnel.

B. SAMPLE CUSTODIAN/RECEIVING TECHNICIAN

1. Responsible for adhering to the policies and procedures set forth in this SOP.

2. Responsible for recommending revisions to the SOP as required to maintain an efficient and reliable operation.

C. DEPARTMENT MANAGER/SUPERVISOR

1. Responsible for ensuring implementation and adherence to this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed by the Analytical Section Department Manager and QAO on an annual basis at a minimum.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer and will include Sample Custodian and Check-In personnel.

VI. GENERAL POLICIES PROCEDURES

A. All procedures following are applicable to sample receiving and Check-In occurring on any shift of any calendar day. (Seven days per week, 24 hours per day).

B. Proposals should be entered into the system before a sample can be logged in on the Auto-invoicing system. If a generic or non-generic proposal is not on the system for the specific client, standard price list is utilized by the system.

C. ROUTINE SAMPLE RECEIPT

1. The Sample Custodian, Project Manager, or Receiving Technician will examine the shipping container and record any damaged incurred through shipping. Any damages noted will be recorded on a Sample Condition Upon Receipt (SCUR) form. An example of this form is included as Attachment 1.

2. Sample Custodian or Sample Receiving technician documents on the SCUR the method of shipment and any tracking numbers.

3. The Sample Custodian or Sample Receiving Technician examines the shipping container and records on the SCUR (enclosed documentation) if Custody Seals are present or absent, intact or broken.

4. The Sample Custodian or Sample Receiving Technician opens the shipping container under a fume hood and determines the condition of the samples. The following observations are recorded on the SCUR.

   a. Temperature upon Arrival:

      1) If a Temperature Blank is present, a thermometer is used to determine the temperature of the blank. The thermometer is allowed to equilibrate in the blank solution for two (2) minutes. The temperature is observed. The temperature is then observed one (1) minute later. If the second temperature is greater than or equal to the first temperature, the first temperature is recorded. If the second temperature is lower, it is recorded.

      2) If no Temperature Blank is present, the presence or absence of coolant, the condition of the coolant, and the condition of the samples are recorded.

   b. Sample pH:

      1) The pH of all preserved samples, except those used to quantify volatile organics, is determined.

      2) A new, glass, disposable pipet is used to withdraw a small portion of sample from the container.

      3) Dispense sample on pH strip.

4) If the pH is higher than 2 (for acid preserved samples) or lower than 10 (for samples preserved with a base), the discrepancy is indicated on the SCUR.

5) The pH of all measured samples is recorded on the Sample Preservation Record (Attachment 6).

c. Container Condition:

1) Containers are examined and any breakage is recorded.

2) Water samples to be analyzed for volatile organics are examined, if headspace is observed it is recorded.

d. Enclosed documentation is reviewed and any discrepancies are noted.

4. Compare the COC records with the shipment received to verify agreement among the information contained on them. If discrepancies are found, contact the PACE Project Manager immediately. If the Project Manager is not available, contact the Quality Assurance Office for further direction.

5. If all samples recorded on the COC records are received by the laboratory and there are no discrepancies observed with the sample shipment, the Sample Custodian or the Check-In Technician will sign the COC record in the 'Received for Laboratory By' box on the document. If problems are noted, sign for shipment and note the problem in the remarks/comments box or reference the SCUR form detailing the problem(s). Route all paperwork, including the Sample and Analysis Data Entry Form (SADEF) (See Attachment 3) to the PM.

6. Enter samples into the LDMS as outlined in Section VI.E.

D. CONTRACT LABORATORY PROGRAM (CLP)

1. The Sample Custodian or Check-In Technician will examine the shipping container and record the following information. One form per case will be used. The form DC-1 (Attachment 4) will be completed as per the instructions found in the latest revision of the 3/90 CLP SOW.

a. Presence/absence of custody seal(s) on the shipping container(s)

b. Condition of custody seal (i.e. intact, broken)

c. Custody seal numbers, when present

d. Presence/absence of airbills or airbill stickers

e. Airbill or airbill sticker numbers

2. The Sample Custodian or Project Manager will open the shipping container, remove the enclosed sample documents, and record on the appropriate form:

a. Presence/absence of EPA custody records

b. Presence/absence of EPA Traffic Reports or Special Analytical Services (SAS) Packing List

c. Condition of sample containers (intact, broken, leaking)

d. Presence/absence of sample tags

e. Sample tag identification numbers

f. Verification of agreement or disagreement of information recorded on receiving documents, (i.e., traffic reports, SAS packing lists) sample containers, sample tags, airbills or bills of lading.

g. Date and time received by laboratory.

3. If sample tags are present:

a. Record the sample tag document control numbers

b. Compare with the COC record(s). If tag numbers are listed, do then match the sample tag numbers received? Document either that these numbers agree or that there is a discrepancy between tag numbers received and those listed on the COC record.

c. Compare the sample identification noted on the tag with the identification noted on the bottle label. Document that this information agrees or that there is a discrepancy between the sample tag and bottle label.

d. If sample tag numbers are not listed on the COC record, record this fact.

5. Document agreement among the forms and any discrepancies found. If discrepancies are found, contact the Document Control Officer (DCO), Project Manager, or the QA office immediately. The DCO or QA representative will contact SMO for clarification and notify the appropriate laboratory personnel.

6. The telephone contact with SMO shall be documented by the person making contact via a CLP Telephone Contact Log provided by SMO-Viar and Company (see Attachment 5). Document the problem(s) and resolution(s).

7. If all samples recorded on the COC record were received by the lab and there are no problems observed with the sample shipment, the Sample Custodian or Check-In Technician will sign the COC record in the 'Received for Laboratory By': box on the document. If problems are noted, sign for shipment and note problems in the remarks box or reference other form(s) detailing the problem(s). The Sample Custodian or Check-In Technician will also sign and date the SAS Packing Lists, Traffic Reports and airbills, if present.

8. Check samples into the LDMS in accordance with Section VI.E.

E. LDMS CHECK IN PROCEDURE

1. From the Menu Screen on the LDMS, press the PF# key which selects the Project Data Entry Screen. After selecting the project data entry screen, select the designated PF key to add projects to the file. If a project number was indicated from a bottle order, select the designated PF key to maintain the project on file. There are five fields on this screen, Client No. (required), Project No (required), alternate bill to (optional), project manager (required), and proposal number. The Client No. is a six digit number that is required to enter samples into the LDMS. The Project No. is a 9 digit number. The first 6 digits will be today's date or the date the project was entered, in YYMMDD format. Outside MN, the first digit will be altered, as explained under 'New Projects' in Section 6 of the Employee SOP manual (see attachments for regions other than MN). The date portion is required for the next screen to work correctly. Leave the last three digits blank to create an analytical project number. The LDMS will take the next available number.

2. Note that the menu at the bottom of the Project Data Entry screen repeats PF4 , PF9, and PF11 from the Menu screen. A PF key is also available for the "Look Up Proposal" option. These keys are not used for adding projects, but allow movement from this screen to others without returning to the Menu screen.

3. To continue adding information for the new project, fill in the client number, PM initials and project number and press Enter.

4. If you enter a client number that does not exist, or a project number that does, you will get an error message.

5. When you enter an existing client number and do not enter an existing project number, the secondary Project Data Entry screen will display.

6. The fields on the Project Data Entry screen will be prefilled if a proposal number has been entered. Fields included are.

   a. Client Name

   b. Client Contact

   c. Alternate Bill To

   d. Client Number

   e. PACE Project Number

   f. Routine Groundwater Number

   g. Project Name or Client Project Number

   h. Client P.O.

   i. Quote

   j. Type

   k. PACE Project Manager

   l. Project Due Date

   m. Project Complete Date

   n. Style Format

   o. Final Report Sent

   p. Project Description

   q. Quoted Amount

7. Check the client name and client contact to make sure they correspond to the COC. Take corrective actions if the fields do not match the information on the form.

8. If data passes an edit check, you will be returned to the project Add Control screen with a confirmation message letting you know the record has been added to the project file. The LDMS will display the project number which has been generated.

9. Information on modification and deletion of project records can be found in the LDMS User's manual.

10. Select the Sample Data Entry Screen to add samples to the displayed project.

11. Each time you exit the Sample Data Entry Screen Add mode, you will have to suppiy a starting sample number. (Safeguards in the LDMS prohibit the use of a sample number more than once. If an existing sample number is inadvertently entered, the computer will search for the next consecutive number available). The Sample Number screen will display. If you have previously added samples for this project since entering this program, you will not have to enter a starting sample number. The last sample number used is saved until you exit to the menu screen.

12. The only field on the Sample Number screen is a 7-digit sample number. This is the PACE assigned sample number. It must be a 7-digit number. Use leading zeros if necessary.

13. When you add samples, the system will assign sample numbers starting with this number, the next available number greater that the numbered entered, or a specific sample number may be assigned. When you finish using this program and exit to the Menu screen, make a note of the last sample number on this screen, and the system will start assigning numbers where it left off.

14. Enter a starting sample number and press enter. The Sample Add screen will display.

15. All fields on the Sample Add screen are modifiable except as noted.

    a. Project Number (required)

    b. Client Number (not modifiable)

    c. (YYQ##) - a sample identifier used for groundwater reporting, showing year, quarter, and serial number.

    d. Field Collected

    e. Collected by (required)

    f. Lab Received (required)

    g. Lab Checked In By (not modifiable)

    h. Sample Due Date (required)

    i. Priority (required)

    j. Sample No. (Leave blank to generate next available number).

k. Sample Description

l. Matrix (required)

m. Bottles (1st field required, others optional)

n. Comments

o. Well Name (required for groundwater projects with a groundwater routine number entered at project level)

p. Subset, Parameter, or Check-in Group Abbreviation (1st field must be entered. Others are optional)

q. QC Type

r. Bottle Labels

s. Billable

t. QC Level

u. Report Format

v. State Sampled In

16. Adding samples to LDMS

a. Press PF9 Sample Add mode

b. Enter Project Number

c. Check Client I.D. to be sure project number is correct

1) If manually entering project number, this will not display until data are keyed and enter is pressed.

d. Enter date collected from COC if known. If unknown, contact PM who in turn will contact the client.

e. Enter "Collected By". If this information is not on the COC, enter "Client". On a regionally specific basis, "Client" may be entered for all samples not collected by PACE, Inc. personnel.

f. Enter sample due date.

g. Enter date received.

h. Leave sample number blank to generate next available number or enter specific sample number if required.

i. Enter Client sample Description.

j. Enter Matrix.

k. Enter priority level which corresponds to pricing only.

l. Enter QC type (if not on proposal). If QC type is not known, leave blank.

m. Billable remains "Yes" unless instructed otherwise.

n. Enter bottle type in first two blanks for bottles. The last three blanks are used for sample location code (see Appendix 1 for Bottle types and storage locations.

(1) Use of this field may be modified on a regionally specific basis, i.e. 2nd and 3rd digits used to designate number of analysis required from the container and 4th digit used to designated a storage location code.

o. Bottle labels default to "Yes" in add mode; "No" in modifying mode. This field is modifiable.

p. Add comments if applicable.

q. Log in analyses for sample.

r. If using specific proposal, required analyses will be automatically displayed (modifiable).

17. Enter data on the Sample Add screen and press Enter.

18. If you entered a check-in group, it will be replaced with abbreviations of its constituent parts (modifiable). Other abbreviations will be moved down to make room. Make sure some abbreviations are not pushed off the screen if check-in group is large.

19. If your data pass the edit check, you will get a confirmation message. A sample record has been written and analysis records have been written for every parameter listed and every parameter in every subset listed for the sample. All of the fields except sample number and well name will remain filled in as an aid in adding additional samples for the same project. The generated sample number appears at the bottom of the screen and should be written near the corresponding sample on the COC.

20. Continue adding samples for one project. Then either press PF13 to add samples for another project or press PF16 to print SCUR and Exit the program to add another project before adding any more samples.

    a. Either PF13 or PF16 will go to the SCUR and cause the SADEF and bottle labels to be printed.

21. To modify or view samples, see the LDMS User's Guide.

VII. ORDER/ENTRY SYSTEM USE

A. Enter proposal number if known.

1. If proposal number is not known or needs verification, check proposal list. Press PF10, Lookup proposal.

2. Search Proposal List by:

    a. Proposal number - PF3
    b. Proposal name - PF5
    c. Proposal by Client Number - PF7
    d. Proposal by Client Name - PF9

3. Select one and fill in blanks. Press appropriate PF key.

4. Proposal will be listed on screen by selection.

5. Selection spaces will be located in bottom left hand corner. Select proposal by entering selection numbers.

    a. PF2-SELECT PROPOSAL - Assigns proposal with project being checked into LDMS

    b. PF3-DISPLAY PROPOSAL - Displays specific information contained in the proposal

    c. Other PF keys move you through the proposal list.

6. After selection is made, press appropriate PF key. If PF2 is selected, proposal will now appear in Proposal number blank on Project Add screen. If PF3 is selected, proposal will be displayed. Pressing Enter will select proposal number. User may exit without selecting.

B. Check in samples following Section VI.E.

VIII. REFERENCES

A. Contract Lab Program (CLP) Statement of Work for Organic and Inorganic Analyses, 3/90 Revision

B. USEPA CLP User's Guide, 12/88 Revision

C. PACE, Inc. LDMS User's Manual, current revision

TABLE III

ANALYTICAL METHODS

Parameter	METHOD EPA	METHOD SW846	Normal Method Detection Limit	EPA Maximum Holding Time
GC/MS Analysis*				
Volatiles				
Water	624		Range	14 days
Soil		8240	Range	14 days
Acid Extractables				
Water	625		Range	7/40
Soil		8250/8270	Range	7/40
Base/Neutral Extractables Without Pesticides/PCB				
Water	625		Range	7/40
Soil		8250/8270	Range	7/40
Pesticide/PCB				
Water	625		Range	7/40
Soil		8250/8270	Range	7/40

NOTE: When Pesticides/PCBs are run in conjunction with Base/Neutral Extracta

* Holding applicable when properly preserved.

Attachment 1

SCUR

Sample Condition upon Receipt

Project Manger Review _____

Project # _____ Proposal # _____

Client _____ Received by / Date: _____

Cooler ID _____

Method of Sample Shipment _____

Control Number (Include Air Bill w/ project paperwork): _____

Yes	No			
☐	○	1	Custody Seals are present and intact.	
☐	○	2	Temperature Blank is present & is acceptable upon arrival: _____ °C	If NO (PM)
			Condition of Coolant: _____	
			Condition of samples: _____	
○	☐	3	Short holding time analyses requested	If YES (PM)
			Analyses: _____	
○	☐	4	Sampled four or more days prior to receipt	If YES (PM)
			Earliest date of sampling: _____	
○	☐	5	Rush Due Date (one week or less) requested.	If YES (RUSH)
			Due Date: _____	
☐	○	6	Sample Containers are intact.	If NO (PM)
			Containers Affected: _____	
☐	○	7	Samples are properly preserved.	If NO (PM)
			See Preservation Record	
☐	○	8	VOA samples are free of head space.	If NO (PM)
			Samples Affected: _____	
☐	○	9	Sample volume appears sufficient.	If NO (PM)

10 Container Labeling Requirements

- ☐ CLP ICOC — ORANGE
- ☐ USATHAMA ICOC — GREEN
- ☐ None
- ☐ Return Sample to Client — GREEN
- ☐ Hazardous Sample — YELLOW

○ (PM) - Contact Project Manager (Phone)
(RUSH) - See "RUSH ANALYSIS PROCEDURE"

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Attachment 2

COC

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THE ASSURANCE OF QUALITY

115325

CHAIN-OF-CUSTODY RECORD
Analytical Request

Report To:

Bill To:

P.O. # / Billing Reference

Project Name / No.

Pace Client No.

Pace Project Manager

Pace Project No.

*Requested Due Date:

Sampled By (PRINT)

Sampler Signature

Date Sampled

ITEM #	SAMPLE DESCRIPTION	TIME	MATRIX	PACE NO.	NO. OF CONTAINERS	PRESERVATIVES: UNPRESERVED	H_2SO_4	HNO_3	VOA			ANALYSES REQUEST	REMARKS
1													
2													
3													
4													
5													
6													

COOLER NOS.	BAILERS	SHIPMENT METHOD OUT / DATE	SHIPMENT METHOD RETURNED / DATE

Additional Comments

ITEM NUMBER	RELINQUISHED BY / AFFILIATION	ACCEPTED BY / AFFILIATION	DATE	TIME

SEE REVERSE SIDE FOR INSTRUCTIONS

Attachment 3

SADEF

DATE: 4/14/92
3:08 PM

P A C E
MINNESOTA REGION

PAGE: 1

Sample and Analysis Data Entry Form - New Sample(s)

PACE Incorporated
Mr. Joe Novotny
1710 Douglas Drive North
Minneapolis, MN. 55422

612-544-5543

Client No : 00010
: Client Contact:
: Address

: Telephone No

Project No: 920414.098 Due Date: 5/26/92 Client P.O. No:
Project Manager: JWJ Project Name: WS030
Manager's Name: Joseph W. Novotny
Project Type: A Analytical
QC Level: 4 Report Style: S
Desc:

Sample No: 10 010789.1 Collected Date: 0/00/00 Collected By: CLIENT
Lab Rec'd Date: 4/14/92 Checked-In By: DRF Priority: 4
Due Date: 5/19/92 Sample Desc: Metals 1
Bottle Types: GN
Comnt: EPA PE SEE TJP FOR SAMPS CNFIRM LOW LVLS BY-U Matrix: LIQUID

Analysis Abbr:	Name:
BA-N	Barium
CD-N	Cadmium
CR-N	Chromium
CU-N	Copper
PB-N	Lead
AG-N	Silver
AS-U	Arsenic
SE-U	Selenium
MET-DIG-N	Metals Digestion
MET-DIG-U	Furnace Metal Digestion

Sample No: 10 010790.5 Collected Date: 0/00/00 Collected By: CLIENT
Lab Rec'd Date: 4/14/92 Checked-In By: DRF Priority: 4
Due Date: 5/19/92 Sample Desc: Metals 2
Bottle Types: GN
Comnt: EPA PE 3 SIG FIGS SEE TJP FOR SAMPLES Matrix: LIQUID

Analysis Abbr:	Name:
SB-N	Antimony
BE-N	Beryllium
NI-N	Nickel
TL-N	Thallium
MET-DIG-N	Metals Digestion

PACE, Inc. reserves the right to return all samples at its discretion.

Attachment 4

DCI

SAMPLE LOG-IN SHEET

Lab Name: _____ Page ____ of ____

Received By (Print Name): _____ Log-in Date: _____

Received By (Signature): _____

Case Number: _____

Sample Delivery Group No.: _____

SAS Number: _____

REMARKS:

1. Custody Seal(s) — Present/Absent* Intact/Broken
2. Custody Seal Nos.: _____ _____
3. Chain-of-Custody Records — Present/Absent*
4. Traffic Reports or Packing List — Present/Absent*
5. Airbill — Airbill/Sticker Present/Absent*
6. Airbill No.: _____ _____
7. Sample Tags — Present/Absent*
   Sample Tag Numbers — Listed/Not Listed on Chain-of-Custody
8. Sample Condition: — Intact/Broken*/ Leaking
9. Does information on custody records, traffic reports, and sample tags agree? — Yes/No*
10. Date Received at Lab: _____
11. Time Received: _____

Sample Transfer

Fraction: _____ _____

Area #: _____ _____

By: _____ _____

On: _____ _____

	CORRESPONDING		
EPA SAMPLE #	SAMPLE TAG #	ASSIGNED LAB #	REMARKS: CONDITION OF SAMPLE SHIPMENT, ETC.

* Contact SMO and attach record of resolution

Reviewed By: _____

Date: _____

Logbook No.: _____

Logbook Page No: _____

FORM DC-1

Attachment 5

Telephone Log

In Reference to Case No(s):

Contract Laboratory Program
REGIONAL/LABORATORY COMMUNICATION SYSTEM

Telephone Record Log

Date of Call: _____

Laboratory Name: _____

Lab Contact: _____

Region: _____

Regional Contact: _____

Call Initiated By: ____ Laboratory ____ Region

In reference to data for the following sample number(s):

_____

_____

_____

Summary of Questions/Issues Discussed:

_____

_____

_____

_____

_____

_____

_____

Summary of Resolution:

_____

_____

_____

_____

_____

_____

_____

_____

_____ _____

Signature Date

Distribution: (1) Lab Copy, (2) Region Copy, (3) SMO Copy

Attachment 6

Sample Preservation Record

Sample Preservation Record

pH of Samples Upon Receipt

Client : _____

Project #: _____

Technician: _____

Date: _____

Page _____ of _____

PM Review _____

Sample Description	Fraction pH by Bottle Type					Comments
	Metals HNO3 <2	Nutrient H2SO4 <2	Cyanide NaOH >12	Sulfide NaOH >9	Hydrocarbons HCl <2	

* Sample pH was adjusted to be compliant with EPA recommendations by _____ date _____

pace, Inc.®

MNINORG FORM MN3106

STANDARD OPERATING PROCEDURE

STANDARDS TRACEABILITY IN THE LABORATORY AND FIELD

SOP NUMBER	MN-P-004-B
AUTHOR	Sue J. Lautt
EFFECTIVE DATE	November 23, 1992
SUPERSEDES	MN-P-004-A

APPROVAL

Field Analytical Supervisor	12-2-92 Date
Inorganic Laboratory Manager	11/24/92 Date
Organic Laboratory Manager	11/30/92 Date
Quality Assurance Officer	12-2-92 Date

TABLE OF CONTENTS

1. PURPOSE

1.1. The purpose of this Standard Operating Procedure (SOP) is to establish a uniform procedure for Standards Traceability in the Laboratory and Field at PACE, Inc.

2. SCOPE/APPLICATION

2.1. Because the proper preparation and storage of analytical standard solutions is of utmost importance, all laboratory and field personnel will follow this protocol for Standards Traceability.

3. RESPONSIBILITIES

3.1. QUALITY ASSURANCE OFFICE (QAO)

3.1.1. The QAO is responsible for monitoring adherence to this SOP.

3.1.2. The QAO is responsible for conducting semi-annual laboratory audits to monitor adherence to this and other SOPs. Results of the audits will be reported to regional management and Corporate QAO.

3.2. DEPARTMENT SUPERVISORS/MANAGERS

3.2.1. The Department Supervisors and/or Managers are responsible for ensuring that the SOP is implemented and followed.

3.3. PERSONNEL

3.3.1. All personnel whose duties require them to handle standards are responsible for adherence to the policies/procedures set forth in this document.

4. REVIEWS/REVISIONS

4.1. This SOP will be reviewed on an annual basis at a minimum.

4.2. At the time of review, any required revisions will be incorporated.

4.3. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

5. DISTRIBUTION

5.1. This SOP will be distributed to the Field Services Manager, Field Laboratory personnel, Laboratory Managers, Laboratory Supervisors, Corporate QAO and to any other areas deemed appropriate by the regional QAO.

6. GENERAL POLICIES AND PROCEDURES

6.1. A bound logbook will reflect a completed record of each prepared standard solution, starting with the pure primary standards and ending with the final working standard solution. Examples of preprinted logbooks are included as Attachments to this document. In some cases, records are maintained using standard laboratory logbooks. All data entries into standard logbooks must include items listed below and must follow documentation guidelines as set forth in PACE, Inc. Standard Operating Procedure MN-L-101, *Documentation in the Laboratory and Field.*

6.2. When preparing primary stock solutions, the following documentation must be included:

6.2.1. Stock standard number
6.2.2. Date of preparation
6.2.3. Analyst's initials
6.2.4. Compound name
6.2.5. Lot number and manufacturer
6.2.6. Purity (97% minimum acceptable purity)
6.2.7. Weights
6.2.8. Dilution volume and solvent
6.2.9. Concentration
6.2.10. Receipt and opened dates for neat compounds
6.2.11. Expiration date

6.3. To prepare an intermediate or working stock solution the following documentation must be included:

6.3.1. Newly assigned standard number
6.3.2. Date of preparation
6.3.3. Analyst's initials
6.3.4. Compound name
6.3.5. Parent solution number
6.3.6. Strength of concentrated stock
6.3.7. Aliquot of concentrated stock (as volume or weight measurement)
6.3.8. Dilution volume and solvent
6.3.9. Final concentration
6.3.10. Expiration date

6.4. All stock, intermediate, and working solutions should be transferred from volumetric flask to appropriate storage containers and stored at the temperatures as specified in the sections following.

6.5. Storage containers must be labeled with solution I.D., concentration, date prepared, expiration data, storage conditions, and initials of preparer. Commonly used labels are included as Attachment 1.

6.6. Semi-volatile organic standards must be monitored for evaporation. The liquid level in the storage container must be marked and noted each time the standard is used.

6.7. All concentrated standard solutions must be replaced depending upon the need, and the stability of the solution.

6.8. Working solutions shall be prepared fresh as specified in the sections following.

6.9. U.S. EPA and USATHAMA standard traceability program requirements are set forth in Appendices 1 and 2 respectively.

6.10. In the following sections, acceptance criteria are provided as advisory limits. These criteria are furnished for the analyst to facilitate monitoring of quality control. In all cases, sound analytical justification may be provided to support data acceptability.

6.11. METALS

6.11.1. Where available, EPA certified/EPA-CRADA certified or A2LA certified standards will be used for the calibration standards and/or the second source standard.

6.11.2. Examples of logbooks/forms used in the metals area are included in Attachment 2.

6.11.3. All metals standards are stored under ambient conditions in limited access areas of the building.

6.11.4. Vendor information/certification is filed in the department supervisor's office. Records are maintained for a minimum of 1 year.

6.11.5. All labeling requirements as detailed in Section 6.3 will be followed.

6.11.6. Shelf life of neat analytes is 1 year or more often as indicated by QC sample results, signs of degradation, etc..

6.11.7. Shelf life of ampules is 1 year from data opened or more often as indicated by QC sample results, signs of degradation, etc..

6.11.8. Shelf life of intermediate standards is 6 months or more often as indicated by QC sample results, signs of degradation, etc.

6.11.9. Working standards shall be prepared daily for furnace analysis and monthly for ICP analysis or more often as indicated by QC sample results, signs of degradation, etc.

6.11.10. Plastic or glass containers are used for storage of standards.

6.11.11. Verification of standards is performed during instrument calibration. A second source solution containing identical analytes of known concentration is analyzed using the calibration curve generated. The results of the second source standard must agree with $\pm$ 10% of the true value.

6.11.12. Absence of contaminants in reagents is assured through the analysis of method blanks.

6.12. GENERAL CHEMISTRY

6.12.1. The general chemistry area performs analysis for a number of parameters. Due to the variance in standards storage requirements, shelf life requirements, acceptance criteria for verification of standards, etc., requirements will be set forth in the method specific standard operating procedures.

6.12.2. Vendor information/certification is filed in the department supervisor's office. Records are maintained for a minimum of 1 year.

6.12.3. Examples of logbooks/forms used in the general chemistry area are included in Attachment 3.

6.12.4. All labeling requirements as detailed in Section 6.3 will be followed.

6.12.5. Absence of contaminants in reagents is assured through the analysis of method blanks.

6.12.6. Plastic or glass containers are used for storage of standards.

6.13. GC VOLATILES

6.13.1. Where available, EPA certified, EPA-CRADA certified, or A2LA certified standards will be used for the calibration standards and/or the second source standard.

6.13.2. Examples of logbooks/forms used in the GC volatiles area are included in Attachment 4.

6.13.3. Copies of vendor information/certification is filed in the QA office. Records are maintained for a minimum of 1 year.

6.13.4. All labeling requirements as detailed in Section 6.3 will be followed.

6.13.5. Standards are stored in a freezer at a temperature of $< 0°$ C.

6.13.6. Expiration dates for neat compounds are provided by the chemical manufacturer or more often as indicated by QC sample results, signs of degradation, etc.

6.13.7. Shelf life of ampules (excluding gases) is 2 months from date opened. Gases are prepared weekly or more often as indicated by QC sample results, signs of degradation, etc.

6.13.8. Working standards will be prepared fresh weekly or more often as indicated by QC sample results, signs of degradation, etc..

6.13.9. Amber, glass containers with Chem-Inert or similar air tight, teflon faced closures are used for storage of standards.

6.13.10. Verification of standards is performed during initial calibration. A second source solution containing identical analytes of known concentration is analyzed using the calibration curve generated for the initial calibration. Control limits will be $\pm$ 25% of the true value until performance base limits are established.

6.13.11. Absence of contaminants in reagents is assured through the analysis of method blanks.

6.14. GC/MS VOLATILES

6.14.1. Where available, EPA certified, EPA-CRADA certified, or A2LA

certified traceable standards will be used for the calibration standards and/or the second source standard.

6.14.2. Examples of logbooks/forms used in the GC/MS volatiles area are included in Attachment 5.

6.14.3. Copies of vendor information/certification is filed in the QA office. Records are maintained for a minimum of 1 year.

6.14.4. All labeling requirements as detailed in Section 6.3 will be followed.

6.14.5. Standards are stored in a freezer at a temperature of < 0° C. Protect the standards from light. Once one of the bottles containing the stock standard solution has been opened, it may be used for no longer than one week.

6.14.6. Expiration dates for neat compounds are provided by the chemical manufacturer. Use of the neat compounds will be discontinued as indicated by QC sample results, signs of degradation, etc..

6.14.7. Shelf life of opened ampules containing components that are gases at room temperature is two months. Shelf life of ampules (excluding gases) is 6 months from date opened or more often as indicated by QC sample results, signs of degradation, etc.

6.14.8. Aqueous standards may be stored for up to 24 hours if held in Teflon-sealed screw-cap vials with zero headspace at 4° C. Protect the standards from light. If not so stored, they must be discarded after one hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept for up to 12 hours in purge tubes connected via the autosampler to the purge and trap device.

6.14.9. Amber, glass containers are used for storage of standards.

6.14.10. Verification of standards is performed during initial calibration. A second source solution containing identical analytes of known concentration is analyzed using the calibration curve generated from the initial calibration. Control limits will be ± 25% of the true value until performance based limits are established.

6.14.11. Absence of contaminants in reagents is assured through the analysis of method blanks.

6.15. GC PESTICIDES/PCBS/HERBICIDES

6.15.1. Semi-volatile organic standards must be monitored for evaporation. The liquid level in the storage container must be marked and noted each time the standard is used.

6.15.2. Where available, EPA certified, EPA-CRADA certified, or A2LA certified standards will be used for the calibration standards and/or the second source standard.

6.15.3. Examples of logbooks/forms used in the GC semivolatile area are included in Attachment 6.

6.15.4. Copies of vendor information/certification is filed in the Department Secretary's office. Records are maintained for a minimum of 1 year.

6.15.5. All labeling requirements as detailed in Section 6.3 will be followed.

6.15.6. Standards are stored in refrigerated storage at 4° C ± 2° C.

6.15.7. Expiration dates for neats may provided by the chemical manufacturer. In cases where no expiration date is supplied, neats will have an expiration date of two years from the date opened. The integrity of the chemical may be verified against a second source after it expires. If agreements between the second source and the expired neat is within ± 10%, the expiration date may be extended for an additional year.

6.15.8. Shelf life of ampules is 1 year from date opened or more often as indicated by QC sample results, signs of degradation, etc.

6.15.9. Working standards will be prepared fresh every 6 months or as needed or more often as indicated by QC sample results, signs of degradation, etc.

6.15.10. Amber, glass containers with Chem-Inert or screw-top, Teflon lined closures are used for storage of standards.

6.15.11. Prior to use of a freshly prepared standard, it is verified against either a second source standard or the standard going out of service. In addition, verification of standards is performed during initial calibration. A second source solution containing identical analytes of known concentration is analyzed using the calibration curve generated from the initial calibration. Control limits will be ± 25% of the true value until performance based

limits are established.

6.15.12. Absence of contaminants in reagents is assured through the analysis of method blanks and lot checks. Reagents lots are checked for routine contaminants on a routine basis. Results of the reagent check are on file with the extraction lab supervisor.

6.16. GC/MS SEMI-VOLATILES

6.16.1. Semi-volatile organic standards must be monitored for evaporation. The liquid level in the storage container must be marked and noted each time the standard is used.

6.16.2. Where available, EPA certified, EPA-CRADA certified, or A2LA certified standards will be used for the calibration standards and/or the second source standard.

6.16.3. Examples of logbooks/forms used in the GC/MS semivolatile area are included in Attachment 7.

6.16.4. Copies of vendor information/certification is filed in the Department Secretary's office. Records are maintained for a minimum of 1 year.

6.16.5. All labeling requirements as detailed in Section 6.3 will be followed.

6.16.6. Standards are stored in a freezer at a temperature of $\leq$ 0° C.

6.16.7. Continuing calibration standards should be prepared weekly and stored at 4° C $\pm$ 2° C.

6.16.8. Expiration dates for neats may provided by the chemical manufacturer. In cases where no expiration date is supplied, neats will have an expiration date of two years from the date opened. The integrity of the chemical may be verified against a second source after it expires. If agreements between the second source and the expired neat is within $\pm$ 25%, the expiration date may be extended for an additional year.

6.16.9. Shelf life of ampules is 1 year from date opened or more often as indicated by QC sample results, signs of degradation, etc.

6.16.10. Working standards will be prepared fresh every 6 months or more often as indicated by QC sample results, signs of degradation, etc.

6.16.11. Amber, glass containers with Chem-Inert or screw-top, Teflon lined closures are used for storage of standards.

6.16.12. Prior to use of a freshly prepared standard, it is verified against either a second source standard or the standard going out of service. In addition, verification of standards is performed during initial calibration. A second source solution containing identical analytes of known concentration is analyzed using the calibration curve generated from the initial calibration. Control limits will be $\pm$ 25% of the true value until performance based limits are established.

6.16.13. Absence of contaminants in reagents is assured through the analysis of method blanks and lot checks. Reagents lots are checked for routine contaminants on a routine basis. Results of the reagent check are on file with the extraction lab supervisor.

6.17. FIELD ANALYTICAL

6.17.1. Where available, EPA certified, EPA-CRADA certified, or A2LA certified traceable standards will be used for the calibration standards and/or the second source standard.

6.17.2. Examples of logbooks/forms used in the field analytical area are included in Attachment 8.

6.17.3. Copies of vendor information/certification is filed in the QA office. Records are maintained for a minimum of 1 year.

6.17.4. All labeling requirements as detailed in Section 6.3 will be followed.

6.17.5. Storage conditions for standards will default to the conditions described in preceding sections depending on the analytical procedures being performed.

6.17.6. Expiration dates for neats are provided by the chemical manufacturer.

6.17.7. Shelf life of ampules (excluding gases) will not exceed the length of the project or will default to the shelf lives described in preceding sections depending on the analytical procedures being performed, whichever is most frequent.

6.17.8. Working standards will be prepared as described in preceding sections

depending on the analytical procedures being performed.

6.17.9. Amber, glass containers are used for storage of standards.

6.17.10. Verification of standards is performed during instrument calibration. A second source solution containing identical analytes of known concentration is analyzed using the calibration curve generated.

6.17.11. Absence of contaminants in reagents is assured through the analysis of method blanks.

7. REFERENCES

7.1. *U.S. EPA Contract Laboratory Program, Statement of Work for Inorganics Analysis, Multi-Media, Multi-Concentration*

7.2. *U.S. EPA Contract Laboratory Program, Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration*

7.3. *U.S. Army Toxic and Hazardous Materials Agency Quality Assurance Program*, January 1990.

7.4. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition*, November 1990.

7.5. All references are to the current issue of the document available at the time the procedure was prepared. As these documents are revised, they will supersede the reference documents. The requirements of the most current approved copy shall be implemented for compliance with the requirements of this procedure.

ATTACHMENT 1 - Labels

PACE REAGENT
Date received / / opened / /
Expiration date / /
Storage condition_____

PACE SOLUTION #_____
Name_____
Date Prep / / Exp. / /
Conc._____
Solvent_____Prep by_____
PACE SOLUTION #_____

ATTACHMENT 2 -Metals Standard Logbook Examples

METALS STANDARD SOLUTION LOG

Element	Stock Conc.	Dilution Factor	Final Conc.	Manufacturer Lot #	Date of Preparation	Standard Number	Analyst Initials	Comments

ATTACHMENT 2 (con't) -Metals Standard Logbook Examples

DATE_____ ELEMENT_____ INST._____ ANALYST_____ BOOK NO._____

TARGET, SPIKES:

AS Pos	Print No.	Sample I.D.	Asb./pk Ht.	Conc.(ppm/ppb)	Comments

ATTACHMENT 3 - General Chemistry Standard Logbook Examples

STANDARD SOLUTION LOG

Date	Analyst	Analyte	Manufacturer	Lot #	Weight or Volume	Final Volume	Final Concentration	Standard Number	Comments

LABFM272

ATTACHMENT 3 (con't) - General Chemistry Standard Logbook Examples

LACHAT STANDARD/INSTRUMENT LOG

Date _____ Conc. Range _____ Gain _____

Analyst _____ Channel _____ # Trays _____

Analyte	MFG	Lot #	Stock Conc.	Volume =>100 mls	Final Conc.	Standard Number	Comments

Date _____ Conc. Range _____ Gain _____

Analyst _____ Channel _____ # Trays _____

Analyte	MFG	Lot #	Stock Conc.	Volume =>100 mls	Final Conc.	Standard Number	Comments

LABFM273

ATTACHMENT 4 - GC Volatiles Standard Logbook Examples

NOTE: The following represent stamps that are used in standard laboratory logbooks.

PREPARATION OF CONCENTRATED STOCK STANDARDS

No _____ Date __/__/__ Chemist _____

Compound _____ Lot No. _____ Purity _____

Gross Wt _____ g
*Tare Wt _____ g
Net Wt _____ g
**Adj. Net Wt _____ mg

Dilution Vol. _____ ml
Concentr. _____ ug/ml

PREPARATION OF STANDARDS OF INTERMEDIARY CONCENTRATION

No _____ Date __/__/__ Chemist _____

Compound _____

Parent Solution Number _____
Strength of Concentrated Stock _____ ug/ml
Aliquot of Concentrated Stock _____ ml
Dilution Volume _____ ml
Final Concentration _____ ug/ml

PREPARATION OF FINAL WORKING STANDARD SOLUTIONS

No _____ Date __/__/__ Chemist _____

Standard Name _____

Compound	Parent Sol. Number	Conc. of Parent Sol. ug/ml	Aliq. Vol. ml	Dilution Vol. (ml)	Final Conc./Sol. ug/ml

VERIFICATION # _____ DATE _____
VENDOR _____ LOT # _____
ORIGINAL CONCENTRATION _____
DILUTION FOR VERIFICATION _____
STANDARD LOG BOOK ID _____
PREPARED BY _____

ATTACHMENT 5 - GC/MS Volatiles Standard Logbook Examples

Book #_____ PACE, Inc. Page # 1 of 100
Standard Preparation Log Book

Std. No.:_____ Date:_____ Analyst:_____

Standard Name:_____

Vendor:_____ Lot #:_____

Compound	Original Conc. ug/mL	Aliq Vol. mL	Dilution Vol.(mL)	Final Conc ug/mL

Std. No.:_____ Date:_____ Analyst:_____

Standard Name:_____

Vendor:_____ Lot #:_____

Compound	Original Conc. ug/mL	Aliq Vol. mL	Dilution Vol.(mL)	Final Conc ug/mL

ATTACHMENT 6 - GC Semivolatile Standard Logbook Examples

NOTE: The following represent stamps that are used in standard laboratory logbooks.

PREPARATION OF CONCENTRATED STOCK STANDARDS

No _____ Date ___/___/___ Chemist _____

Compound _____ Lot No. _____ Purity _____

Gross Wt _____ g
*Tare Wt _____ g
Net Wt _____ g
**Adj. Net Wt _____ mg

Dilution Vol. _____ ml
Concentr. _____ ug/ml

PREPARATION OF STANDARDS OF INTERMEDIARY CONCENTRATION

No _____ Date ___/___/___ Chemist _____

Compound _____

Parent Solution Number _____
Strength of Concentrated Stock _____ ug/ml
Aliquot of Concentrated Stock _____ ml
Dilution Volume _____ ml
Final Concentration _____ ug/ml

PREPARATION OF FINAL WORKING STANDARD SOLUTIONS

No _____ Date ___/___/___ Chemist _____

Standard Name _____

Compound	Parent Sol. Number	Conc. of Parent Sol. ug/ml	Aliq. Vol. ml	Dilution Vol. (ml)	Final Conc./Sol. ug/ml

VERIFICATION # _____ DATE _____
VENDOR _____ LOT # _____
ORIGINAL CONCENTRATION _____
DILUTION FOR VERIFICATION _____
STANDARD LOG BOOK ID _____
PREPARED BY _____

ATTACHMENT 7 - GC/MS Semivolatile Standard Logbook Examples

PACE INC. - BNA 9

Mixture Identifications

ATTACHMENT 7 (con't) - GC/MS Semivolatile Standard Logbook Examples

PACE INC. BNA 11

Title: Preparation of Calibration Standards

I. Preparation of SOM 2/88 Stock Solution

Components and Concentration		Amount Added
A.	Methylene chloride	Z[1] x 100 uL
B.	Internal Standard, 2000 ug/mL	20 uL
C.	Acid Surrogate Mix, 2000 ug/mL	80 uL
D.	Base Surrogate Mix, 1000 ug/mL	160 uL
E.	Polynuclear Aromatic Hydrocarbons Mix, 2000 ug/ml	80 uL
F.	Base-Neutrals Mix 1, 2000 ug/mL	80 uL
G.	Base-Neutrals Mix 2, 2000 ug/mL	80 uL
H.	Benzidines Mix, 2000 ug/mL	80 uL
I.	Hazardous Substance Mix 1, 2000 ug/mL	80 uL
J.	Hazardous Substance Mix 2, 2000 ug/mL	80 uL
K.	Phenols Mix, 2000 ug/mL	80 uL
L.	Pesticide Mix, 2000 ug/mL	80 uL
		Z ml of 160 ug/mL solution

II. Working Calibration Solutions

For the following solution:

		Stock[2]	$MeCl_2$[3]
A.	160 ppm standard	200 uL	0 uL
B.	120 ppm standard	150 uL	50 uL
C.	80 ppm standard	100 uL	100 uL
D.	50 ppm standard	50 uL	110 uL
E.	20 ppm standard	25 uL	175 uL

[1] Z is the number of milliliters of stock desired
[2] Stock solution prepared in Step I.
[3] $MeCl_2$ is prefortified with Internal Standard at 40 ug/mL.

ATTACHMENT 7 (con't) - GC/MS Semivolatile Standard Logbook Examples

PACE INC. BNA 12

Title: Preparation of Calibration Standards

I. Preparation of SOM 3/90 Stock Solution

Vendor	Solution Name	Sol'n #	Conc (ug/mL)	Amount Added
Rester	SV Calibration Mix #1	31007	2000	80 uL
	SV Calibration Mix #2	31008	2000	80 uL
	SV Calibration Mix #3	31009	2000	80 uL
	SV Calibration Mix #4	31010	2000	80 uL
	SV Calibration Mix #5	31011	2000	80 uL
	SV Calibration Mix #7	31013	2000	80 uL
	3,3-Dichlorobenzidine	31026	2000	80 uL
	Acid Surrogate Standard Mix	31003	2000	80 uL
	B/N Surrogate Standard Mix	31004	1000	160 uL
	SV Tuning Compound	31001	2500	64 uL
	SV Internal Standard	31006	2000	10 uL
-	MeCl	-	-	126 uL
			Total Volume:	1000 uL

II. Working Calibration Solutions for SOM 3/90:

Sol'n Name	Conc. Standard (mg/mL)	Stock Added Added (uL)	$MeCl_2$[1] Added (uL)	Final Vol. (uL)
SSTD 160	80	80	80	160
SSTD 120	60	60	100	160
SSTD 080	40	40	120	160
SSTD 050	25	25	135	160
SSTD 020	10	10	150	160

(1) $MeCl_2$ is prefortified with Internal Standard at 20 ug/mL.

ATTACHMENT 7 (con't) - GC/MS Semivolatile Standard Logbook Examples

PACE INC. BNA 25

PREPARATION OF INITIAL CALIBRATION STANDARD SOLUTIONS

No_____ Date__/__/____ Chemist_____

Standard Name_____

Compound	Parent Sol. Number	Conc. of Parent Sol. ug/ml	Aliq.Vol. ml	Mixture Number	Final Conc./Sol. ug/ml

Confirmation File ID_____

ATTACHMENT 7 (con't) - GC/MS Semivolatile Standard Logbook Examples

PACE INC. BNA 47

PREPARATION OF WORKING STANDARDS

No_____ Date__/__/____ Chemist_____

Standard Name_____

Compound	Parent Sol. Number	Conc. of Parent Sol. ug/ml	Aliquot Volume	Final Volume	Final Concentration

Diluted with: _____

Calculations Verified By_____

No_____ Date__/__/____ Chemist_____

Standard Name_____

Compound	Parent Sol. Number	Conc. of Parent Sol. ug/ml	Aliquot Volume	Final Volume	Final Concentration

Diluted with: _____

Calculations Verified By_____

ATTACHMENT 8 - Field Analytical Standard Logbook Examples

Book #_____ PACE, Inc. Page # 1 of 100
Standard Preparation Log Book

Std. No.:_____ Date:_____ Analyst:_____

Standard Name:_____

Vendor:_____ Lot #:_____

Compound	Original Conc. ug/mL	Aliq Vol. mL	Dilution Vol.(mL)	Final Conc ug/mL

Std. No.:_____ Date:_____ Analyst:_____

Standard Name:_____

Vendor:_____ Lot #:_____

Compound	Original Conc. ug/mL	Aliq Vol. mL	Dilution Vol.(mL)	Final Conc ug/mL

APPENDIX 1

1. CLP ANALYTICAL STANDARDS REQUIREMENTS

1.1. OVERVIEW

1.1.1. The U.S. Environmental Protection Agency will not supply analytical reference standards either for direct analytical measurements or for the purpose of traceability. All contract laboratories will be required to prepare from neat materials or purchase from private chemical supply houses those standards necessary to successfully and accurately perform the analyses required in the latest revision of the CLP Statement of Work.

1.2. PREPARATION OF CHEMICAL STANDARDS FORM THE NEAT HIGH PURITY BULK MATERIAL

1.2.1. A laboratory may prepare their chemical standards from neat materials. Commercial sources for neat chemical standards pertaining to compounds listed on the Compound Target List are given in the Appendix C of the *Quality Assurance Materials Bank: Analytical Reference Standards*, Seventh Edition, January 1988. Laboratories should obtain the highest purity possible when purchasing neat chemical standards. Standards purchased at less that 97% purity must be documented as to why a higher purity could not be obtained.

1.2.2. Neat chemical standards must be kept refrigerated when not being used in the preparation of standard solutions. Proper storage of neat chemicals is essential in order to safeguard them from decomposition.

1.2.3. The purity of a compound can sometimes be misrepresented by a chemical supply house. Since knowledge of purity is needed to calculate the concentration of solute in a solution standard, it is the contract laboratory's responsibility to have analytical documentation ascertaining that the purity of each compound is correctly stated. Purity confirmation, when performed, should use either differential scanning calorimetry, gas chromatography with flame ionization detection, high performance liquid chromatography, infrared spectrometry, or other appropriate techniques. Use of two or more independent methods is recommended. The correction factor for impurity when weighing neat materials in the preparation of solution standards is:

$$\text{Weight of impure compound} = \frac{\text{Weight of pure compound}}{(\text{percent purity}/100)} \qquad \text{Equation 1}$$

where "weight of impure compound" is that required to prepare a specific volume of a solution standard of a specified concentration.

1.2.4. Mis-identification of compound occasionally occurs and it is possible that a mislabeled compound may be received from a chemical supply house. It is the contract laboratory's responsibility to have analytical documentation ascertaining that all compounds used in the preparation of solution standards be correctly identified. Identification confirmation, when performed, should use gas chromatographic/mass spectrometry analysis on at least two different analytical columns, or other appropriate techniques.

1.2.5. Calculate the weight of material to be weighed out for a specified volume taking into account the purity of the compound and the desired concentration. A second person must verify the accuracy of the calculations. Check balances for accuracy with a set of standard weights. All weighing should be performed on an analytical balance to the nearest 0.1 mg and verified by a second person. The solvent used to dissolve the solute should be compatible with the protocol in which the standard is to be used. The solute should be soluble, stable, and nonreactive with the solvent. In the case of a multi-component solution, the components must not react with each other.

1.2.6. Transfer the solute to a volumetric flask and dilute to the specified solution volume with solvent after ensuring dissolution of the solute in the solvent. Sonication or warming may be performed to promote dissolution of the solute. This solution is to be called the primary standard and all subsequent dilutions must be traceable back to the primary standard.

1.2.7. Log notebooks are to be kept for all weighing and dilutions. all subsequent dilutions from the primary standard and the calculations for determining their concentrations are to be recorded and verified by a second person. all solution standards are to be refrigerated when not is use. All solution standards are to be clearly labeled as to the identity

of the compound or compounds, concentration, data prepared, solvent, and initials of the preparer.

1.3. PURCHASE OF CHEMICAL STANDARDS ALREADY IN SOLUTION

1.3.1. Solutions of analytical reference standards can be purchased by the Contractors provided they meet the criteria set forth in sections following.

1.3.2. Laboratories must maintain the following documentation to verify the integrity of the standard solutions they purchase:

1.3.2.1. Mass spectral identification confirmation of the neat material
1.3.2.2. Purity confirmation of the neat material
1.3.2.3. Chromatographic and quantitative documentation that the solution standard was QC checked according to the following section.

1.3.3. The Contractor must purchase standards for which the quality is demonstrated statistically and analytically by a method of the supplier's choice. One way this can be demonstrated is to prepare and analyze three solutions; a high standard, a low standard, and a standard at the target concentration (see 1.3.4.1 and 1.3.4.2 following). The supplier must then demonstrate that the analytical results for the high standard and low standard are consistent with the difference in theoretical concentrations. This is done by the Student's t-test in section 1.3.4.6. If this is achieved, the supplier must then demonstrate that the concentration of the target standard lies midway between the concentrations of the low and high standards. This is done by the Student's t-test in section 1.3.4.7. Thus, the standard is certified to be within 10 percent of the target concentration.

1.3.4. If the procedure in 1.3.3 is used, the supplier must document that the following have been achieved:

1.3.4.1. Two solutions of identical concentration must be prepared independently from neat materials. An aliquot of the first solution must be diluted to the intended concentration (the "target standard"). One aliquot is taken from the second solution and diluted to a concentration ten percent greater than the target standard. This is called the "high standard".

One further aliquot is taken from the second solution and diluted to a concentration 10 percent less than the target standard. This is called the "low standard".

1.3.4.2. Six replicate analyses of each standard (a total of 18 analyses) must be performed in the following sequence: low standard, target standard, high standard, low standard, target standard, high standard. . . .

1.3.4.3. The mean and variance of the six results for each solution must be calculated.

$$\text{Mean} = (Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6)/6 \qquad \text{Equation 2}$$

$$\text{Variance} = (Y_1^2 + Y_2^2 + Y_3^2 + Y_4^2 + Y_5^2 + Y_6^2 - [(6)(\text{Mean})^2]/5 \qquad \text{Equation 3}$$

1.3.4.4. The values Y_1, Y_2, Y_3, . . ., represent the results of the six analyses of each standard. The means of the low, target, and high standards are designated M_1, M_2, and M_3, respectively. The variances of the low, target, and high standards are designated V_1, V_2, and V_3, respectively. Additionally, a pooled variance, V_p, is calculated.

$$V_p = (V_1/0.81 + V_2 + V_3/1.21)/3 \qquad \text{Equation 4}$$

1.3.4.5. If the square root of V_p is less than one percent of M_2, then $M_2^2/10{,}000$ is to be used as the value of V_p in all subsequent calculations.

1.3.4.6. The test statistic (TS) must be calculated:

$$TS = |(M_3/1.1) - (M_1/0.9)|/(V_p/3)^{0.5} \qquad \text{Equation 5}$$

If the test statistic exceeds 2.13, then the supplier has failed to demonstrate a twenty percent difference between the high and low standards. In such a case, the standards are not

acceptable.

1.3.4.7. The test statistic (TS) must be calculated:

$$TS = |M_2 - (M_1/1.8) - (M_3/2.2)|/(V_p/4)^{0.5} \quad \text{Equation 6}$$

If the test statistic exceeds 2.13, the supplier has failed to demonstrate that the target standard concentration is midway between the high and low standards. In such a case, the standards are not acceptable.

1.3.4.8. The 95% confidence intervals for the mean results of each standard must be calculated:

$$\text{Interval for Low Standard} = M_1 \pm (2.13)(V_p/6)^{0.5} \quad \text{Equation 7}$$

$$\text{Interval for Target Standard} = M_2 \pm (2.13)(V_p/6)^{0.5} \quad \text{Equation 8}$$

$$\text{Interval for High Standard} = M_3 \pm (2.13)(V_p/6)^{0.5} \quad \text{Equation 9}$$

These intervals must not overlap. If overlap is observed, then the supplier has failed to demonstrate the ability to discriminate the 10 percent difference in concentrations. In such a case, the standards are not acceptable.

1.3.4.9. In any event, the laboratory is responsible for the quality of the standards employed for analyses under this contract.

1.4. DOCUMENTATION OF THE VERIFICATION AND PREPARATION OF CHEMICAL STANDARDS

1.4.1. It is the responsibility of each laboratory to maintain the necessary documentation to show that the chemical standards they have used in the performance of CLP analysis conform to the requirements previously listed. Weighing logbooks, calculations, chromatograms, mass spectra, etc., whether produced by the laboratory or purchased from chemical

supply houses, must be maintained by the laboratory and may be subject to review during On-Site inspection visits. In those cases where the documentation is supportive of the analytical results of data packages sent to EPA, such documentation is to be kept on file by the laboratories for a period of one year.

1.4.2. Upon request by the Technical Project Officer or Administrative Project Officer, the Contractor shall submit their most recent previous year's documentation (12 months) for the verification and preparation of chemical standards within 14 days of the receipt of request to the recipients he/she designates.

1.4.3. The Agency may generate a report discussing deficiencies in the Contractor's documentation for the verification and preparation of chemical standards or may discuss the deficiencies during an On-Site laboratory evaluation. In a detailed letter to Technical Project Officer, Administrative Project Officer, and EMSL-LV, the Contractor shall address the deficiencies and the subsequent corrective action implemented by the Contractor to correct the deficiencies within 14 days of receipt of the report or the On-Site laboratory evaluation. An alternate deliver schedule may be proposed by the Contractor, but it is the sole decision of the Agency, represented either by the Technical Project Officer or Administrative Project Officer, to approve or disapprove the alternate delivery schedule. If an alternate delivery schedule is proposed, the Contractor shall describe in a letter to the Technical Project Officer, Administrative Project Officer, and the Contracting Officer why he/she is unable to meet the delivery schedule listed in this section. The Technical Project Officer/Administrative Project Officer will not grant an extension for greater than 14 days for the Contractor's response letter to the standards documentation report. The Contractor shall proceed and not assume that an extension will be granted until so notified by the TPS and/or APO.

1.4.4. If new SOPs are required to be written or SOPs are required to be amended because of the deficiencies and the subsequent corrective action implemented by the Contractor, the Contractor shall write/amend and submit the SOPs per the requirements listed in Exhibit E, Section III of the U.S. EPA CLP Statement of Work.

1.4.5. If the Contractor fails to adhere to the requirements listed here, a Contractor may expect, but the Agency is not limited to the following actions: reduction of number of samples sent under the contract, suspension of sample shipment to Contractor, GC/MS tape audit, data package audit, an On-Site laboratory evaluation, a remedial laboratory evaluation sample, and/or contract sanctions, such as a Cure Notice.

APPENDIX 2

1. USATHAMA CALIBRATION CHECK STANDARDS

1.1. REQUIREMENTS FOR USE

1.1.1. Calibration check standards are required for all Class 1 and 1B methods and shall be analyzed during recertification and with each initial certification. The calibration check standard shall contain all analytes of interest for the method in question at a concentration near the upper end of the calibration range. Results of the calibration check standards shall fall within the limits of acceptability as described in Section 1.2 following.

1.2. LIMITS OF ACCEPTABILITY

1.2.1. CASE 1. A certified check standard is available from the EPA or some other source with both the true value and limits of acceptability specified by the supplier. The results must fall within the limits specified by the supplier, or ± 10% for inorganics and within ± 25% for organics, whichever is less.

1.2.2. CASE 2. A certified check standard is available from the EPA or some other source with a true value specified but without limits of acceptability. The results must fall within ±10% for inorganics and within ± 25% for organics.

1.2.3. CASE 3. If no certified check standard is available, the contractor laboratory shall prepare a check standard using a second source of reference material. This standard shall be prepared by a different analyst than the one who prepared the calibration standard. If weighing of the material is required, a different balance should be used, if possible. The results must fall within ± 10% for inorganics and within ± 25% for organics.

1.2.4. CASE 4. If there is only one source of reference material available, then the calibration and calibration check standards must be prepared from the same material. The standards shall be prepared by different analysts. If weighing is required, different balances should be used, if possible. The results must fall within ± 10% for inorganics and within ± 25% for organics.

1.2.5. For all cases listed above, after the seventh acceptable calibration check standard, the limits of acceptability shall be ± two standard deviations, as determined from the first seven points.

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STANDARD OPERATING PROCEDURE

Internal Chain of Custody

SOP NUMBER	MN-L-103-D
AUTHOR	Steve Crupi
EFFECTIVE DATE	January 19, 1994
SUPERSEDES	MN-L-103-C

APPROVAL

Manager, Inorganic Laboratory — Date 1/19/94

Quality Assurance Officer — Date 1/19/94

TABLE OF CONTENTS

I. PURPOSE

A. The purpose of this Standard Operating Procedure (SOP) is to establish uniform procedures for logging samples into and out of storage, for internal custody transfers and for interregional transfer. Specific contractual obligations regarding internal chain of custody will supersede the procedures set forth in this document.

B. Internal chain of custody is established to provide unbroken tracking of the sample from the time it is received into the facility until the time of final disposition.

C. Internal chain of custody procedures as set forth in this document will be applied to projects requiring strict sample tracking in accordance with project contracts and to "routine" projects requiring minimal tracking.

II. RESPONSIBILITIES

A. PERSONNEL

1. All employees checking a sample out of storage for any reason are responsible for adherence to this SOP.

2. Employees are responsible for contacting their supervisor or the Quality Assurance Office with any required revisions to this SOP.

B. SAMPLE CUSTODIAN/CHECK-IN PERSONNEL

1. Sample Custodians are responsible for ensuring that samples received are properly logged into assigned storage areas.

C. DEPARTMENT SUPERVISOR/MANAGER

1. The department supervisor/manager is responsible for ensuring adherence to the policies and procedures set forth in this SOP.

2. The department supervisor/manager is responsible for providing adequate resources to allow the policies and procedures set forth in this SOP to be performed.

D. QUALITY ASSURANCE OFFICE

1. The Quality Assurance Office is responsible for monitoring adherence to this SOP.

2. The Quality Assurance Office is responsible for implementing all required revisions to this SOP.

3. The Quality Assurance Office is responsible for determining distribution of this SOP and maintaining distribution records for this and other SOPs.

III. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum. Any required revisions will be incorporated into the SOP at the time of review.

IV. DISTRIBUTION

A. Distribution of this document will be determined by the Quality Assurance Office.

V. GENERAL POLICIES

A. The laboratories are restricted access areas. Access to the building is through a monitored reception area. In the MN Region, doors to the laboratory are accessible only by entering a code to unlock the door.

B. Visitors must register in a visitor's book in the reception area and be escorted while in the building. All visitors are required to wear identification badges.

C. Special instances may arise where an individual is not available to relinquish custody (e.g.- when separate shifts are preparing samples, or an analyst with custody calls in sick) and sample processing must continue. To deal with these situations and maintain sample integrity, an analyst assumes custody of a sample lot by ensuring that custody has not been broken and documenting this on the COC form. The explanation on the COC form might read, "I assumed custody of lot ABC from Jane Doe. The extracts were locked in the refrigerator with no evidence of tampering" and you would sign as receiver with the date, time, and purpose for your assuming custody. These occurrences will be kept to a minimum (prior arrangements should be made for custody transfer if someone knows they will be unavailable).

D. In order to facilitate assembly of data packages, log book numbers and pages used may be included on a list in the data package.

E. Regionally specific chain of custody procedures are included as Appendix I.

F. STRICT INTERNAL CHAIN OF CUSTODY

1. Internal chain of custody of samples and sample extracts/digestates for CLP, HAZWRAP, USATHAMA and other regulated programs must be maintained within the laboratory in addition to the field chain of custody received with the samples and maintained by the project manager. The following protocol (and referenced forms) are to be used by sample preparation personnel or analysts in obtaining samples and by analysts in obtaining samples or extracts/digestates for analysis.

   a. Samples and extracts/digestates are stored in designated secure areas. Samples are to be transferred to secure storage as soon as possible after receipt. Storage location for samples is given in PACE, Inc. SOP number MN-C-701. Extracts are stored in a secure refrigerator located in the extraction lab or in secure refrigerators located in the organic instrument laboratories. Digestates are stored in secure rooms located in the inorganic laboratory. Refrigerators, freezers, and other sample storage areas are kept locked during non-business hours. Regular business hours are from 8:00 am to 4:45 pm Monday through Friday. If an analyst is present, locking storage areas is not necessary.

   b. Only the Sample Custodians or designated personnel have access to the secure storage area(s).

   c. Samples and extracts/digestates remain in secure storage until removed for further sample preparation or analysis.

d. Bound Sample Control Record (SCR) books will be maintained for each type of project requiring internal COC. The books will be assigned a unique number, be paginated, and the book number will be written on each page. See Attachment 1 for an example of the SCR logbook page.

G. ROUTINE INTERNAL CHAIN OF CUSTODY

1. All transfers of samples into storage will be documented on an internal chain of custody (COC) record. An example of the internal COC record used for this procedure is included as Attachment 3.

2. Samples requiring routine internal chain of custody will be inventoried on the Internal Chain of Custody form.

3. All applicable information will be filled in the appropriate section of the form.

4. Any additional custody procedures will be addressed on a regionally specific basis.

VI. PROCEDURE

A. All samples are inventoried in the appropriate SCR book as they are put into a secure storage area. When samples are needed for analysis, the analyst notifies the Sample Custodian (or designee) and the following information is recorded in the SCR book (Attachment 1):

1. This section is to be completed by the Sample Custodian as sheets are originated through the completion of the project.

2. Sample Number (required)

   a. The unique LDMS laboratory sample number assigned at receipt. Enter the individual number or first and last number for a consecutive series of samples.

3. Relinquished by/Received by (required)

   a. The initials of the individual relinquishing the samples and the initials of the individual receiving the samples must be entered in this column.

   b. In the case of relinquishing or receiving custody from a storage area, the appropriate columns will be completed.

4. Date and Time Removed/Date and Time Returned (required)

   a. This column contains the date and time the samples are relinquished and received by the Sample Custodian.

5. Reason (required)

   a. This column is used to record the reason for removing the samples from the secure area.

   b. If custody is changed within a department without returning the sample/fraction(s) to secure storage, this will be documented in this column. For internal transfers, include the initials of the person relinquishing custody, the person assuming custody and the time when the transfer occurred.

   c. Codes may be used to indicate reason for transfer.

B. Upon completion of sample preparation, the extracts/digestates are logged into either the Sample Extract Control Logbook or the Sample Digestate Control Logbook according to the extract/digestate ID number. See Attachment 2 and 4 for an example of each of these logbook pages. Extracts are kept for 365 days or the number of days required by specific contracts.

C. All transfers of samples and extracts/digestates into and out of storage will be documented in their respective logbooks.

1. The control records for samples are maintained by the Sample Custodian (or designated personnel).

2. After a sample has been removed from storage by the Sample Custodian and relinquished to the analyst (or the analyst assumes custody from a cooler), the analyst is responsible for the custody of the sample. Each analyst must return the samples to the storage area. The applicable logbook pages must be again initialed by the analyst and the Sample Custodian to transfer custody.

3. If an Internal Department Transfer of samples is necessary, this is documented in the Reason Column.

VII. REFERENCES

A. Contract Lab Program (CLP) Statement of Work of Organic and Inorganic Analyses.

B. USEPA CLP User's Guide.

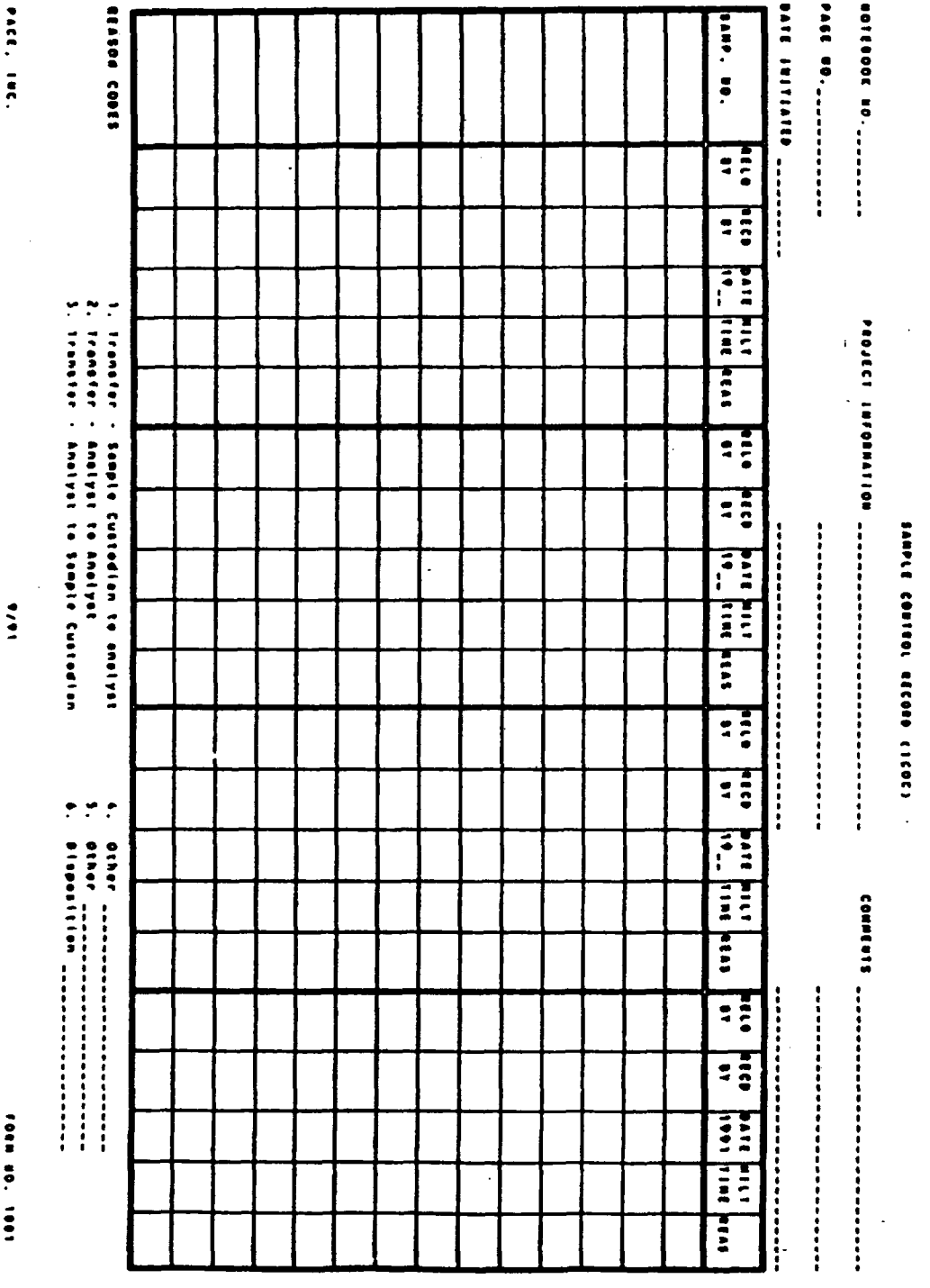
C. U.S. Army Toxic and Hazardous Materials Agency's Quality Assurance Program.

VIII. ATTACHMENTS

A. Regionally specific attachments are included in this document. Appendices specific to regional protocols/procedures are also included.

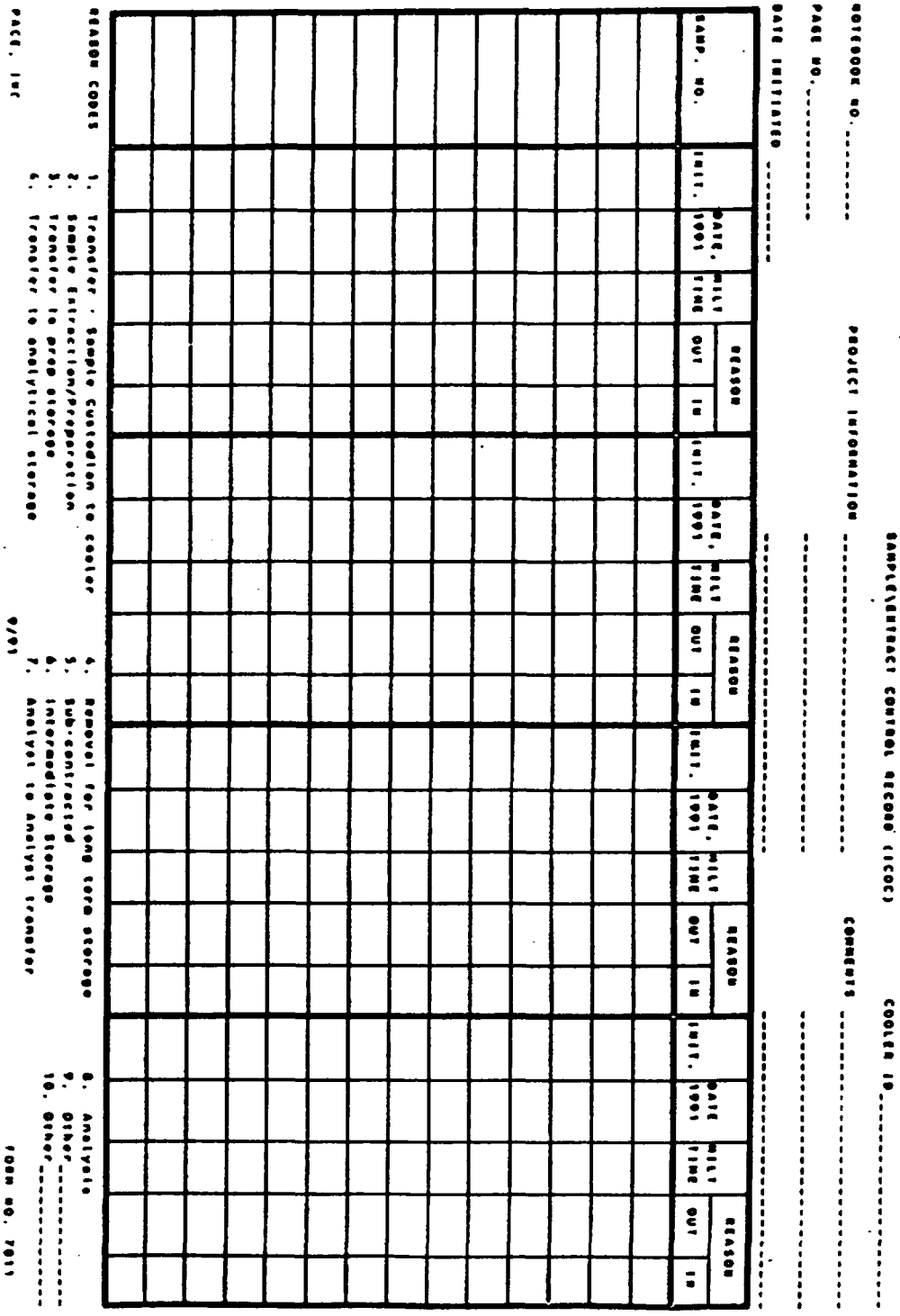
Attachment 1

Sample Control Record



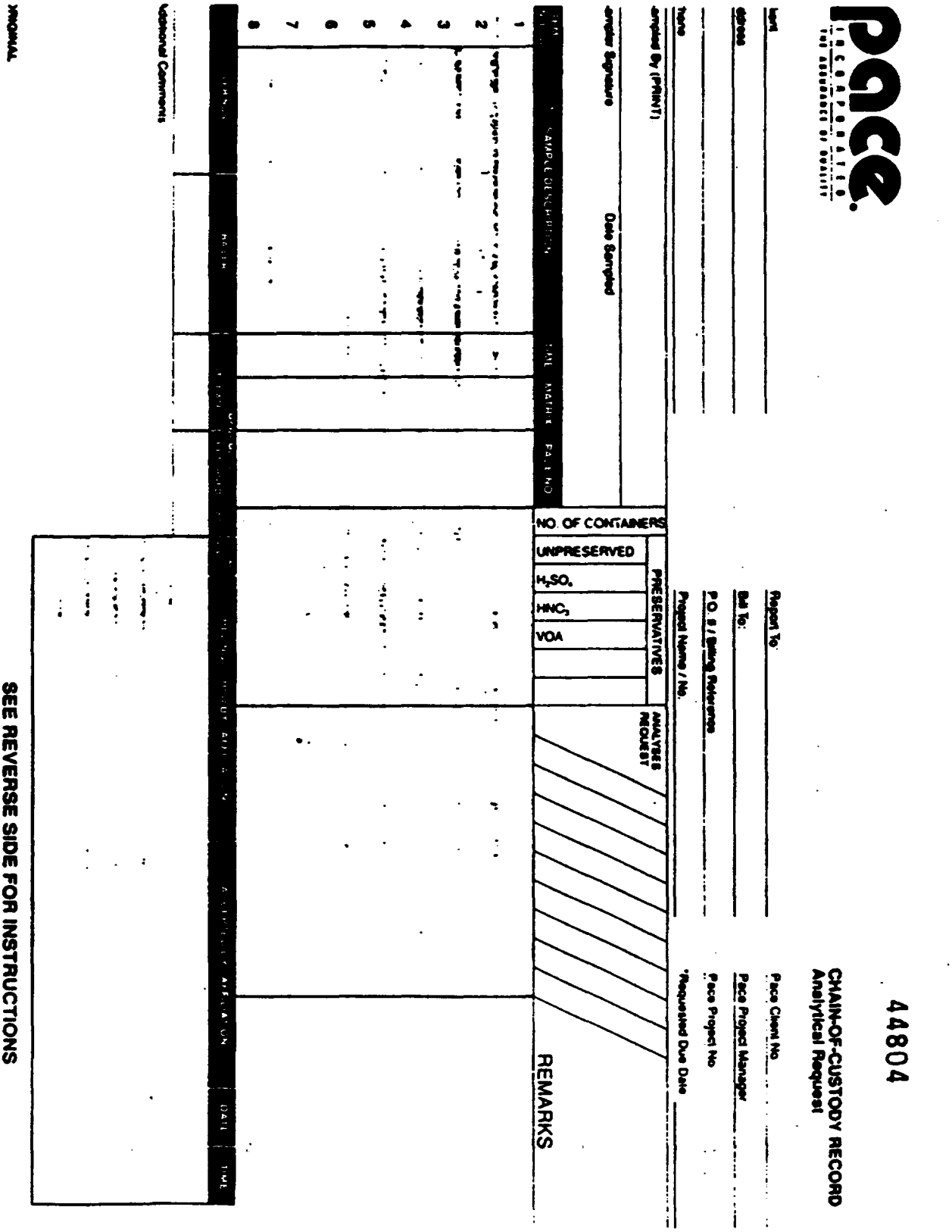
Attachment 2

Sample Extract/Digestate Control Record



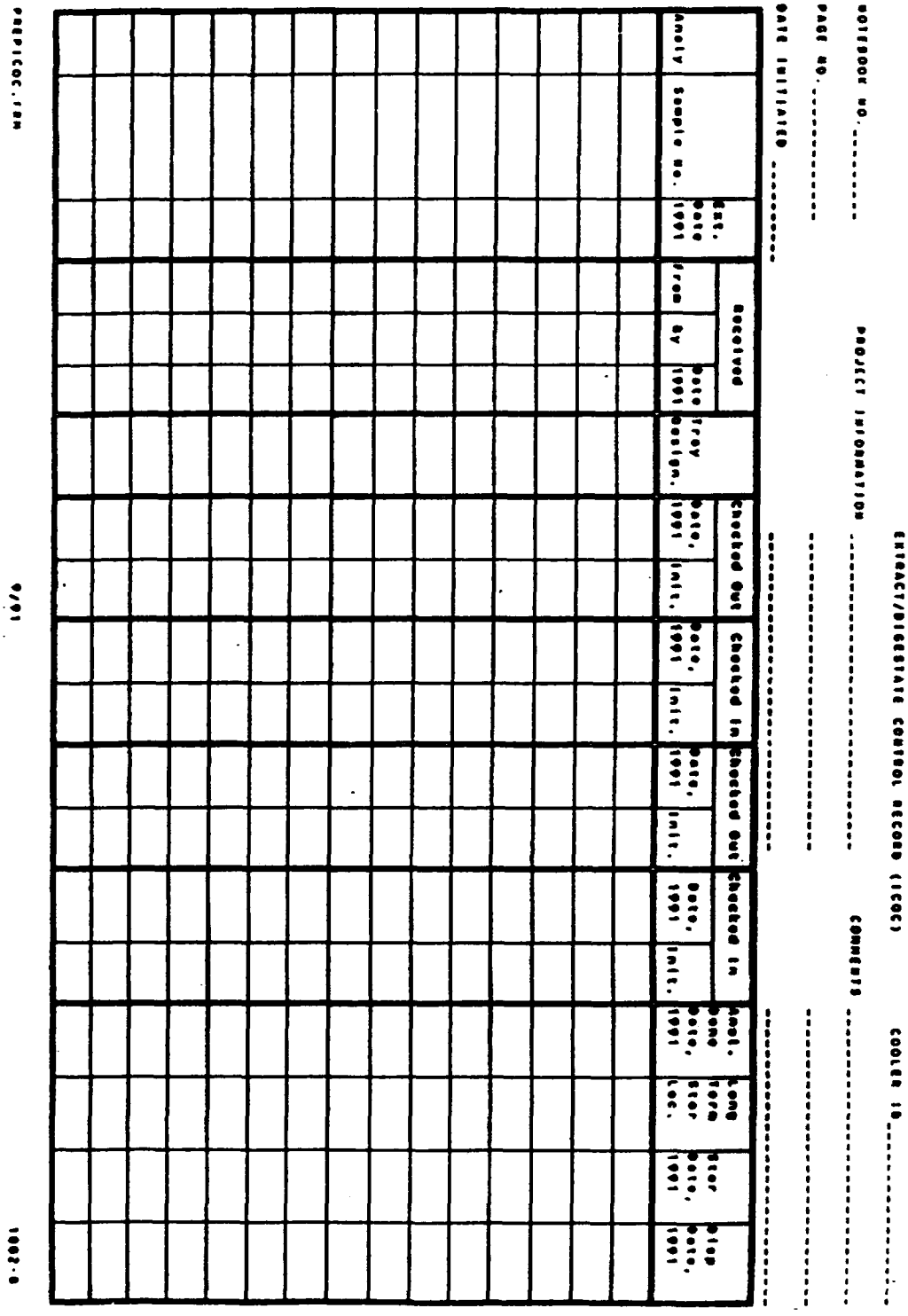
Attachment 3

Internal Chain of Custody Form



Attachment 4

Extract/Digestate Control Record



APPENDIX I

I. CUSTODY TRANSFER UPON SAMPLE RECEIPT

A. A Check-in technician accepts custody of samples upon receipt by signing, dating, and noting time of receipt on the Field Chain of Custody or other documents containing sample information.

B. After samples have been logged into the Laboratory Data Management System (LDMS), the Check-in technician relinquishes custody of the samples to the sample custodian via a second entry on the Field Chain of Custody or other appropriate document(s).

1. If lack of information or time constraints prohibit the Check-in technician from logging in the samples the same day they are received, the technician relinquishes custody of the sample to "locked storage" via a second entry on the Field Chain of Custody or other appropriate document(s).

2. When the samples can be logged into the LDMS, a Check-in technician accepts custody from "locked storage" via a third entry on the Field Chain of Custody or other appropriate document(s).

C. The sample custodian routes samples to appropriate laboratory coolers, as indicated by the last number of the storage location code on the container label.

1. Storage areas are delineated as follows:
   001: Cooler C1
   002: Cooler C2
   003: Cooler C4
   004: Cooler C4
   005: Cooler C7
   006: Cooler C6

007: Cooler 013, non-routine samples
Cooler 05, routine samples
008: Metals storage M1
009: Asbestos Laboratory
000: Miscellaneous, as indicated in sample comments

2. If storage space is not available in the designated area, the sample custodian informs a Check-in technician and the storage code is changed to an area where the sample can be stored.

D. The sample custodian makes an entry in a Custody book designated to a storage area for each container placed in that storage area.

1. The custodian enters the sample number, followed by the container type.

2. If more than one of a container type is present in the sample, they are entered separately, with each entry delineated by sequential numbers after the container type.

3. The custodian enters the date and time each container was placed in storage, initials each entry, and enters the reason for transfer. A single line cross out is made through the "Time Out" column.

4. The first and second numbers in the sample storage code indicate the number of analyses to be performed on the container. The sample custodian allots enough space in the Custody book for the required transfers.

5. After the containers are entered into the Custody book, the laboratory responsible for the corresponding storage area, has custody of the samples.

E. When an analyst removes a container to perform an analysis, she/he accepts custody of the container.

1. The analyst enters the date and time the container was removed, enters the reason for removal, and initials the entry.

2. When the container is returned to storage, the analyst enters the time in the "Time In" column.

3. If custody is transferred to another analyst before the container is returned to storage, this transfer is noted in the "Reason" column of the Custody book.

4. If the entire sample in the container is used, the analyst enters CWNR (Sample Consumed will not return) for the time returned.

F. After all analyses are completed on a container, it is transferred to an appropriate long term storage area.

1. A custodian enters the date and time the sample was removed in the Laboratory Custody book.

2. The entry is initialed. The reason is listed as "Removal for long term storage." A single line cross is made through the "Time In" column.

3. The container is logged in the Long Term Storage Custody book appropriate to the area where the sample is being stored.

G. When a sample disposal or return occurs, the custodian notes the occurrence in the Custody book for the appropriate cooler from which the sample was taken.

1. Date and time out are entered and the entry is initialed.
2. The reason is listed as "Disposal" or "Returned to Clients," and a single line cross is made through the "Time In" column.

H. When containers are sent to a sub-contracting laboratory, the container is signed out of the storage area (an entry similar to when a sample is returned to the client) and the reason is listed as "Sub-contracted."

II. GENERAL CUSTODY BOOK PROCEDURES

A. Each book contains information about containers in only one storage area.

B. The date entries first made on a page is listed at the top of the page.

C. The PACE project numbers corresponding to each container on a page are listed at the top of the page.

APPENDIX II

SAMPLE CUSTODIANS:

	FIRST SHIFT	SECOND SHIFT
Alternate	Paul Ernst	

APPENDIX III

Internal Chain of Custody of Extracts
GC and GC/MS Semivolatile Areas
Metals Area

The following is the sequence of how extracts will move and be documented in the semivolatile and metals area.

1. A prep lab person will deliver extracts/digestates and place them in assigned storage locations. He/she will fill out columns a, b, c, e and f of the attached form.

2. An analyst will verify that all of the samples are there and initials for received by (column d).

3. When the analyst is ready to perform the analysis, he/she checks the samples out of the storage area. Date and initial columns g and h. During samples analysis, samples will be stored in refrigerator B for pesticides/herbicides, refrigerator 08 for BNAs, and the metals instrument lab for metals.

4. When analysis is completed, the analyst will check the samples back into the appropriate storage location (completes columns j and k). At this time, all dilutions will also be checked in.

   a. Enter the sample number with a (dl) appended behind it and the dilution made. EX. 10 30000ldl 1:100b. enter date and person checking in (columns i and j).

5. When sample data are validated, the date analysis completed will be entered by the supervisor (column k).

6. Once a week, a designated lab-tech will go through the storage locations and remove all samples that have a date analysis completed entered. CLP, Hazwrap and USATHAMA organic extracts will be sent back to the prep lab for long term storage. All regular organic client extracts will be placed in autosampler vial boxes. Each box will be numbered and will have a beginning sample and ending sample date (columns l and m). These boxes will be stored in the designated storage location until they are three months old.

7. Once the ending date on a long term storage box is 3 months old, the samples extracts will be discarded (complete column n).

8. All standards will be stored in refrigerator C in the pesticide/herbicide area and cooler 08 in the BNA area. Metals standards will be stored in the metals instrument lab. No standards will be placed in refrigerators A or B.

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STANDARD OPERATING PROCEDURE

Discrepancy Reports/Corrective Action

SOP NUMBER	**MN-P-001-E**
AUTHOR	**Joe Novotny**
EFFECTIVE DATE	**August 10, 1993**
SUPERSEDES	**MN-P-001-D**

APPROVAL

for RCS
Regional Director 08/11/93 **Date**

Quality Assurance Officer 08/11/93 **Date**

1 PURPOSE

1.1 The purpose of this Standard Operating Procedure (SOP) is to provide a detailed explanation of the procedure used to prepare, distribute, and act upon discrepancy reports.

2 APPLICATION

2.1 The policies and procedures contained in this SOP are to be applied when discrepancies arise during the course of sampling, receipt, analysis, reporting, or other PACE, Inc. activity.

2.2 All employees are responsible for the proper use of discrepancy reports and subsequent corrective actions.

3 GENERAL POLICIES

3.1 The Quality Assurance Office will maintain records of discrepancy reports.

3.2 A discrepancy is any disagreement or divergence from what is expected.

3.3 All discrepancies must be documented so corrective actions can be taken to prevent any future occurrences.

3.4 All discrepancy reports will be reviewed on a twice monthly basis by the discrepancy quality performance team (QPT) or Quality Assurance Officer.

4 RESPONSIBILITIES

4.1 PERSONNEL

4.1.1 The individual encountering the discrepancy will be responsible for initiating the Discrepancy Report (DR) and assuring that the information provided in the DR is complete and thorough.

4.1.2 The initiator will be responsible for addressing the discrepancy with his/her department supervisor/manager, then routing the DR to the Project Manager (PM).

4.2 QUALITY ASSURANCE PERSONNEL

4.2.1 Responsible for preparation and distribution of DR summary reports.

4.2.2 Responsible for maintaining DR records.

4.2.3 Responsible for coordinating the QPT.

4.2.4 Responsible for verifying that corrective actions have been inplemented.

4.3 PROJECT MANAGER

4.3.1 Responsible for assuring that the client is notified when necessary, that appropriate documentation accompanies the final report, and the discrepancy gets reported to the Quality Assurance Office.

4.3.2 Responsible for completing the DR and returning it to the Quality Assurance Office.

4.4 SECTION SUPERVISORS, DEPARTMENT MANAGERS

4.4.1 Responsible for periodic review of DR summary reports.

4.4.2 Work with the initiator to implement corrective actions.

4.4.3 Assist the PM when required to assure that appropriate corrective action is provided.

4.4.4 Responsible for ensuring that this SOP is implemented.

4.4.5 Responsible for ensuring that required modifications to this SOP are communicated to the QAO.

4.5 DISCREPANCY QPT

4.5.1 A Discrepancy QPT may be assigned at the discretion of the region.

4.5.2 The Discrepancy QPT will consist of members representing various areas of the region. The areas represented may include Field Services, Sample Check-in, Client Services, Organic Chemistry, Inorganic Chemistry, Quality Assurance and any other area involved in the generation or resolution of discrepancies.

4.5.3 Representatives will participate on the Discrepancy QPT for a six month period. Reappointment will be an option.

4.5.4 Representatives will be appointed by the Quality Assurance Office in conjunction

with department managers.

4.5.5 The Discrepancy QPT is responsible for identifying problem areas and providing recommendations to prevent reoccurrence.

4.5.6 The Discrepancy QPT will be responsible for ensuring that discrepancies are brought to closure in a manner consistent with quality standards.

5 - DISTRIBUTION

5.1 This SOP will be distributed to all sections that are subject to discrepancy occurrences.

6 REVIEW PROCESS AND REVISIONS

6.1 This SOP will be reviewed annually at a minimum by a representative of the Quality Assurance Office.

6.2 If required, revisions will be made at the time of review by the representative of the Quality Assurance Office.

6.3 Suggestions or recommendations for revisions to this SOP will be directed to the Region Quality Assurance Office or the Department Manager.

6.4 First level approval for this SOP will be made by the Quality Assurance Officer or his designee. Second level approval for this SOP will be made by the Regional Director or his designee.

7 PROCEDURE

7.1 RESOURCES

7.1.1 Attachment 1: Sample Preservation Discrepancy Report

7.1.1.1 This form is representative of the form to be used when the discrepancy involves a problem in the preservation of samples (as indicated by pH level).

7.1.1.2 In some regions, preservation discrepancies may be addressed using the Discrepancy Report Form described in Section VII.2.

7.1.2 Attachment 2: Discrepancy Report Form

7.1.2.1 This form is representative of the form to be used for all other

discrepancies. Broken sample containers, receipt of a different number of samples than anticipated, samples received on days other than that anticipated, analytical problems, reporting problems, sampling problems, scheduling problems, and other occurrences require the notification of the project manager and need to be documented.

7.1.2.2. A discrepancy code will be applied to the report. The codes are available on the reverse side of the Discrepancy Report Form. Typical codes are included as Attachment 3.

7.1.3 Codes are assigned on a regionally specific basis. Regions may at there discretion, use other types of report forms specific to various departments/activities.

7.2 DESCRIPTION OF PROCEDURE

7.2.1 Sample Preservation Discrepancies

7.2.1.1 Laboratory personnel will record the information requested on the form (see Attachment 1) for any sample which is not properly preserved, as indicated by pH level.

7.2.1.2 The form is routed to the appropriate project manager so the client can be notified.

7.2.1.3 The Quality Assurance Office will review the sample preservation discrepancy forms on a bi-weekly basis.

7.2.2 Other Discrepancies

7.2.2.1 As soon as possible following the discovery of a discrepancy, the form will be completed as fully as possible by the person first encountering the discrepancy.

7.2.2.2 Upon preliminary completion of the DR, the Initiator will obtain a DR number from the Quality Assurance Office or designated department. The DR number can be obtained by contacting the Quality Assurance Office or designated department or by taking the appropriate number from a DR clipboard located in the designated department.

7.2.2.3 Upon completing the initiator section, the department manager/supervisor initials are required.

7.2.2.4 The completed form will be routed to the PM as soon as possible.

7.2.2.5 The initiator will exercise judgment in determining whether other personnel need to be notified at this point in the routing sequence.

7.2.2.6 The PM will review the form. The review will include the following:

7.2.2.6.1 The initial screening will include a form completeness check, assurance that the discrepancy is explained adequately, and review of corrective action if applicable.

7.2.2.7 The PM will route the appropriate sections of the form to the Quality Assurance Office. Routing of the forms should be done at the earliest possible time.

7.2.2.8 The Project Manager will assure that appropriate corrective action is taken.

7.2.2.9 Appropriate corrective action may include client contact. All PM comments should be recorded along with client comments. See Section 8 for an outline of corrective action steps.

7.2.2.10 The Project Manager will complete his/her portion of the form and route the completed form to the Quality Assurance Office.

7.2.2.11 The PM will communicate with the initiator the proposed corrective action as soon as the action is determined.

7.2.2.12 The Quality Assurance Office will review the discrepancy, route copies to the initiator and manager/supervisor, and work with departments to ensure that corrective actions are implemented.

7.2.3 The Quality Assurance Office will prepare a monthly or quarterly discrepancy report summary and distribute this summary to Department Managers, the Regional Director, and Corporate QA.

7.2.4 The Quality Assurance Office will archive the forms.

8 CORRECTIVE ACTION

8.1 See Attachment 3 for a flow chart of the corrective action process.

8.2 If, as a result of audits or QC sample analyses, methods systems prove to be unsatisfactory, corrective action shall be implemented. The project manager, department manager, Quality Assurance Officer, supervisor, and analyst may be involved in the corrective action. If previously reported data are affected by a situation requiring correction or if the corrective action impacts a project budget or schedule, the action will directly involve the project manager (and Quality Assurance Officer).

8.3 For immediate or long-term corrective actions, steps comprising a closed-loop corrective action system are as follows:

8.3.1 Define the problem.

8.3.2 Assign responsibilities for problem investigation.

8.3.3 Determine if the condition is significant.

8.3.4 Investigate and determine the cause of the problem.

8.3.5 Sample Analysis Discrepancy

8.3.5.1 Check all calculations

8.3.5.2 Re-analyze the sample

8.3.5.3 Verify the integrity of the spiking solution, laboratory control sample, or calibration standard.

8.3.5.4 Check instrument and operating conditions to preclude the possibility of malfunctions or operator error.

8.3.6 Systems Discrepancy

8.3.6.1 Evaluate impact on related items or activities.

8.4 Determine the corrective action(s) necessary to eliminate the problem.

8.5 Assign and accept responsibilities for implementing the corrective action.

8.6 Establish the effectiveness of the corrective action and implement the correction.

8.7 Verify and document that the corrective action has eliminated the problem (using the Discrepancy Report form).

8.8 Depending upon the nature of a problem, the corrective action implemented may be formal or informal. In either case, occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated must be documented.

8.9 In addition, if the corrective action mandates the preparation of a new standard or calibration solution(s), a comparison study between the new solution versus the old solution will be performed. The results are supplied with the weekly QC submittal as verification of problem elimination.

8.10 The archives of discrepancy reports will be maintained for a period of one year.

9 REFERENCES

9.1 USEPA *Good Automated Laboratory Practices (DRAFT), Recommendations for Ensuring Data Integrity In Automated Laboratory Operations*, December 28, 1990.

9.2 USEPA Contract Laboratory Program, *Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration*, Document OLM01.

9.3 PACE, Inc. Laboratory Quality Assurance Plan.

9.4 ASME, NQA-1-1989 Edition, *Quality Assurance Program Requirements for Nuclear Facilities*.

9.5 All references are to the current issue of the document available at the time the procedure was prepared. As these documents are revised, they will supersede the reference documents. The requirements of the most current approved copy shall be implemented for compliance with the requirements of this procedure.

	Initials	Date
Initiator:		
PM:		
QA:		

ATTACHMENT 1

Sample Preservation Discrepancy

Sample #	Project #	Analysis	Date Analyzed	Client	pH	P.M.

ATTACHMENT 2

PACE, INCORPORATED DISCREPANCY REPORT

DR.No. _____
(Obtain from QA)
DR.Code:_____
QA USE: _____/_____

routing sequence

		signature sequence Initial	Date
Initiator		_____	_____
Super.	____	_____	_____
PM	____	_____	_____
QA	____	_____	_____

(INITIATOR)

CLIENT:_____ P.M._____
ANALYSIS:_____ PROJECT #: _____
SAMPLE(s):_____

DISCREPANCY:

PROPOSED RESOLUTION:

(PROJECT MANAGER)

CLIENT CONTACT: YES ( ) NO ( ) DATE: _____
PM COMMENTS:

CLIENT/QA COMMENTS

ATTACHMENT 2, CONTINUED

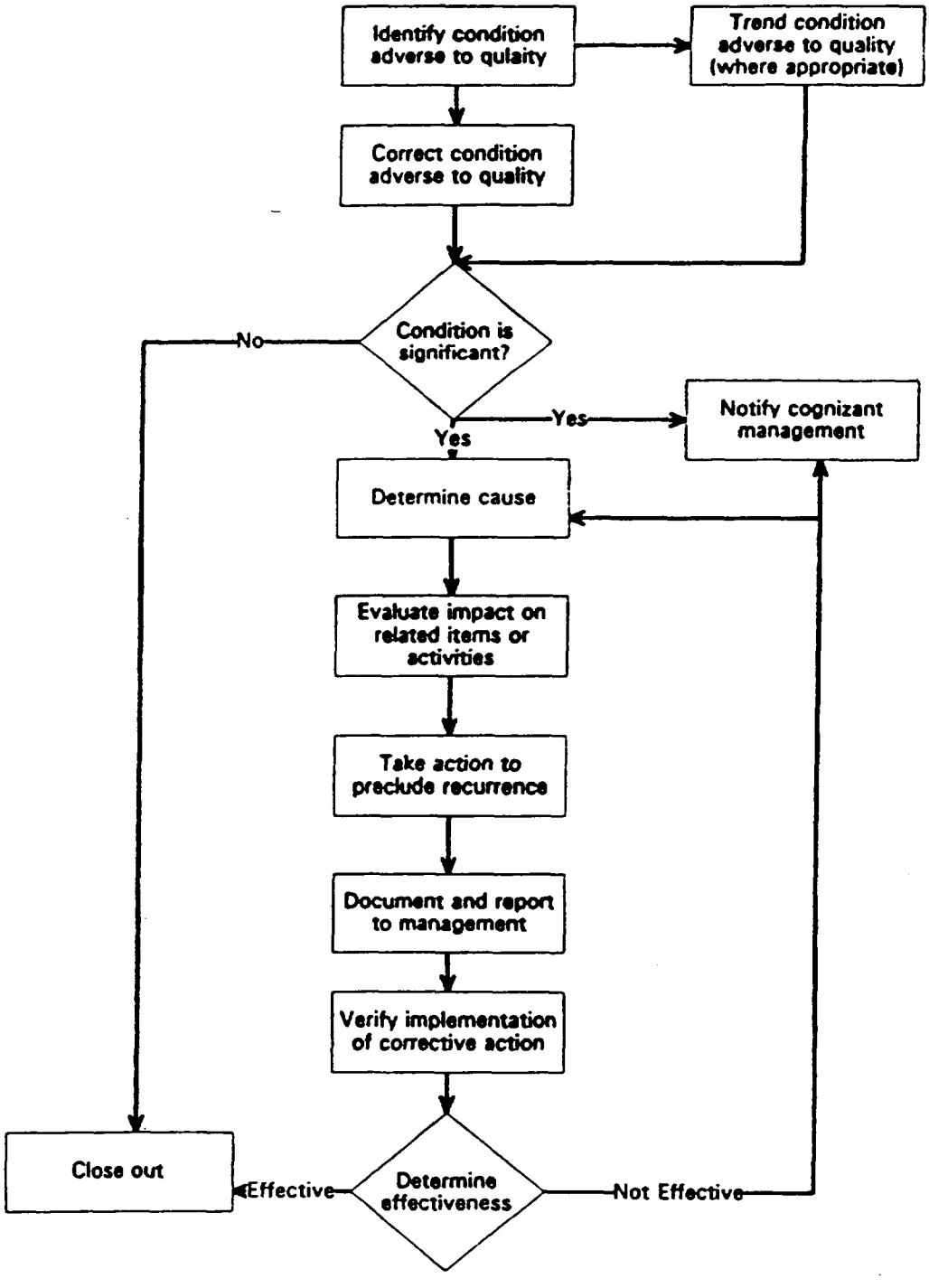
DISCREPANCY REPORT PROCEDURE

1. The initiator completes the top half of the form.
2. The initiator obtains a discrepancy report (DR) number from Quality Assurance (QA)by using the clipboard used to assign numbers and summarize DRs.
3. The initiator writes the "Dr No." in the upper left hand corner of the form.
4. The initiator takes the form to their supervisor for initialization. The form then gets forwarded to the project manager.
5. The project manager fills out the bottom half, writing notes on the form and contacts the client if needed.
6. The project manager writes any comments and resolutions on the form.
7. The project manager routes a copy to the initiator or verbally notifies the initiator of the resolution to the discrepancy. The original form is forwarded to QA.

DISCREPANCY CODES

1. Holding Time
   - 1.0 Checked in out of holding
   - 1.1 Dilution run out off holding
   - 1.2 Arrived out of holding
   - 1.3 Short holding time parameter sample arrived after hours
   - 1.4 Arrived after >50% of holding time had expired
   - 1.5 Miscellaneous
   - 1.6 Holding time not applicable
   - 1.7 PACE error
2. Lost Samples
   - 2.0 Checked in out of holding
   - 2.1 Sample misplaced during analysis
   - 2.2 Miscellaneous
3. Preservation
   - 3.0 Not preserved
   - 3.1 Inadequately preserved
4. Sample Volume
   - 4.0 Insufficient sample provided
   - 4.1 Insufficient sample as a result of analysis
   - 4.2 Headspace present
   - 4.3 Extract final volume suspect
5. Lab Accident
   - 5.0 As a result of check-in/storage
   - 5.1 During analysis
6. Contamination
7. Q.C. Outlier
   - 7.0 Matrix
   - 7.1 Spiking error
   - 7.2 Instrumental
   - 7.3 Preparation problem
   - 7.4 Control Chart Outlier
8. Improper check-in of sample
   - 8.0 Client error
   - 8.1 PACE error
9. Nonproject Related
   - Discrepancy (i.e. cooler out of control)
10. Miscellaneous

ATTACHMENT 3



CORRECTIVE ACTION FLOW CHART

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INCORPORATED
THE ASSURANCE OF QUALITY

STANDARD OPERATING PROCEDURE

Performance and System Audits

SOP NUMBER	MN-Q-206-B
AUTHOR	Joe Novotny
EFFECTIVE DATE	January 18, 1994
SUPERSEDES	MN-Q-206-A

APPROVAL

Regional Director — Date 1/19/94

ACCEPTANCE

Quality Assurance Officer — Date 1/19/94

1 PURPOSE

1.1 This Standard Operating Procedures (SOP) sets forth the policies and procedures governing the performance and response to external and internal audits.

2 SCOPE/APPLICATION

2.1 The policies and procedures set forth in this document are applicable to all personnel participating in or responding to external and/or internal audits.

3 RESPONSIBILITIES

3.1 LABORATORY MANAGEMENT

3.1.1 Laboratory management is responsible for ensuring that the standards described in this document are implemented and adhered to.

3.1.2 Laboratory management will provide the necessary resources, facilities, and equipment that may be required; receive and respond to QA reports and audits; and provide all other laboratory personnel with the guidance, training, or supervision they require to perform successfully in their assigned roles.

3.2 QUALITY ASSURANCE OFFICE (QAO)

3.2.1 The QAO is responsible for review of system SOPs, inspection and audit of the system, review of reports for data integrity, and review of control limits.

3.3 PERSONNEL

3.3.1 All personnel are responsible for familiarity with and conformity to SOPs.

4 REVIEWS/REVISIONS

4.1 This SOP will be reviewed on an annual basis at a minimum.

4.2 At the time of review, any required revisions will be incorporated and the superseded document replaced.

5 DISTRIBUTION

5.1 Distribution of this SOP will be determined by the Quality Assurance Office.

5.2 Distribution records will be maintained by the Quality Assurance Office.

6 PERFORMANCE AND SYSTEM AUDITS

6.1 PACE'S SYSTEM AUDITS

6.1.1 Internal Audits:

6.1.1.1 All records, logs, and data files are audited quarterly for completeness, accuracy, and adherence to standard operating procedures by an internal auditing team. Audit team members include the Quality Assurance Officer and any other associated personnel. Several random project files are evaluated for compliance to procedures throughout the analytical process (i.e., from sample receipt through the final report). Supervisors, and lab analysts routinely check all records for the same criteria.

6.1.2 External Audits:

6.1.2.1 PACE is audited as required by regulatory agencies to maintain laboratory certifications, and by various commercial clients with laboratory auditing programs. These audits include: USEPA, USATHAMA, AIHA, and other appropriate federal, state and private agencies.

6.1.3 Total Quality System Audit:

6.1.3.1 The Corporate Quality Office performs a yearly on-site audit at each regional facility. The Corporate audit is conducted by Corporate Quality. This audit is designed to evaluate all regional office operations and is not limited to only laboratory operations. Audits may either be systems-related or technical in nature, depending on the type of information needed for making quality improvements.

6.2 PERFORMANCE EVALUATIONS:

6.2.1 PACE participates in the US EPA semi-annual drinking water (WS Series) and semi-annual wastewater (WP Series) Performance Evaluation Studies (four studies per year).

6.2.2 PACE participates in various client-sponsored performance evaluations by analyzing QC samples prepared and submitted by commercial clients in conjunction with their own QA program.

6.2.3 Several government proficiency samples are analyzed annually to maintain

various laboratory certification.

6.2.4 PACE regional offices are provided blind QC check samples quarterly. These are provided by Corporate Quality as a part of the PACE Interregional Testing Survey, and may also be provided independently by the regional Quality Assurance Officer.

7 REFERENCES

7.1 Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, US EPA Contract Laboratory Program.

7.2 All references are to the current issue of the document available at the time the procedure was prepared. As these documents are revised, they will supersede the reference documents. The requirements of the most current approved copy shall be implemented for compliance with the requirements of this procedure.

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COPY #6

STANDARD OPERATING PROCEDURE

ANALYSIS OF WHOLE AIR SAMPLES COLLECTED IN SUMMA (TM) PASSIVATED CANISTERS FOR VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY, EPA METHOD TO-14

SOP NUMBER	MN-0-~~458~~ 460A
AUTHOR	Steve Sanders
EFFECTIVE DATE	June 14, 1993
SUPERSEDES	First Issue

APPROVALS

Steven P. Sanders
Air Analytical Supervisor — 08/27/93 Date

Manager Air Analytical — 8/27/93 Date

Quality Assurance Officer — 8/27/93 Date

TABLE OF CONTENTS

Page No.

I. PURPOSE

The purpose of this Standard Operating Procedure is to provide quality control and analytical guidance for the analysis of whole air samples contained in SUMMA (TM) passivated canisters using gas chromatography/mass spectrometry. This SOP is based on EPA Compendium Method TO-14 and EPA Contract Laboratory Program (CLP) SOW No. XXX - Ambient Air.

II. SCOPE/APPLICATION

A. SCOPE

This procedure is designed to analyze volatile organic compounds (VOCs) that have been found to be stable when collected in SUMMA (TM) polished stainless steel canisters. Table 1 lists target VOCs applicable to this method. A 500 cc aliquot of the whole air sample is concentrated prior to gas chromatographic (GC) separation and mass spectrometry full scan detection. Samples expected to contain VOCs in a range of 1 part per billion by volume (ppbv) to 250 ppbv can be analyzed by this technique. Source level samples that may contain part per million by volume (ppmv) contaminants are analyzed utilizing a different means of sample concentration (PACE SOP No. MN-0-457-AH).

B. SAFETY

The toxicity of carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. A current awareness file of OSHA regulations regarding the safe handling of the chemicals specified and a reference file of material safety data sheets is maintained in the laboratory and is available to all personnel involved in the chemical analysis.

III. RESPONSIBILITY

A. QUALITY ASSURANCE OFFICER

1. The Quality Assurance Officer has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

2. The Quality Assurance Officer will conduct semiannual audits of the facility to monitor adherence to this and other SOPs. The results of the audit will be reported to Regional Management and Corporate Quality.

B. ORGANIC LABORATORY MANAGER/SECTION SUPERVISOR

1. The manager/supervisor is responsible for ensuring adherence to this SOP.

2. The manager/supervisor will ensure that this SOP is reviewed on an annual basis.

3. The manager/supervisor will ensure that the Quality Assurance Officer is notified when revisions to the SOP are required.

C. ANALYST

1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated and the superseded document replaced.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer.

B. Distribution records will be maintained by the Quality Assurance Officer.

VI. PROCEDURE

A. DEFINITIONS

1. Absolute canister pressure = Pg + Pa, where Pg = gauge pressure in the canister (kPa, psig) and Pa = barometric pressure.

2. Absolute pressure - Pressure measured with reference to absolute zero as opposed to atmospheric pressure, usually expressed as kPa, mm Hg or psia.

3. Cryogen - A refrigerant used to obtain very low temperatures in the gas chromatographic oven. A typical cryogen is liquid nitrogen (bp - 195.8°C).

4. Dynamic calibration - Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

5. Gauge pressure - Pressure measured above ambient atmospheric pressure as opposed to absolute pressure. Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

6. MS-SCAN - The GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run. As used in the current context, this procedure serves a qualitative identification and characterization of the sample.

7. Megabore(TM) column - Chromatographic column having an internal diameter (I.D.) greater than 0.50 mm. The Megabore(TM) column is a trademark of the J&W Scientific Co. For purposes of this SOP, Megabore(TM) refers to chromatographic columns with 0.53 mm I.D.

8. Qualitative accuracy - The ability of an analytical system to correctly identify compounds.

9. Quantitative accuracy - The ability of an analytical system to correctly measure the concentration of an identified compound.

B. MATERIALS, SUPPLIES, AND EQUIPMENT NEEDED

1. Standard preparation materials.

   a. 10, 25, 50, 100, 250, 500, and 1000 uL gas tight syringes (Hamilton).

   b. Supelco custom standard mixes in methanol at 20 mg/mL and Chem Serv individual neat standards or equivalent.

   c. Burdick and Jackson purge and trap grade methanol.

   d. Various sizes of class A glass volumetric flasks.

   e. SUMMA(TM) passivated canisters, six liter capacity and 40 psig maximum pressure.

   f. Zero grade air high pressure cylinder.

   g. 0-1 SLPM electronic mass flow controller with controller.

   h. 25 mL sparge vessel for humidification purposes.

   i. Laboratory designed flash evaporator consisting of a 1/4" x 10" stainless steel SUMMA(TM) passivated tubing wrapped with heat wrap. One end is fitted with a Swagelock(TM) tee for a zero grade inlet and septum cap. The other end fits directly onto the canister.

   j. Heat controller capable of heating and maintaining a temperature of 180°C.

   k. Bubble flow meter to aid in setting the zero grade air flow at 1000 mL/min.

2. Analytical instrumentation.

   a. Hewlett Packard 5890 Series I gas chromatograph with packed column mass flow controller and SGE metal jet separator.

   b. J & W Scientific DB-624 30m x 0.53mm Megabore(TM) column.

c. Chromatographic grade high pressure helium cylinder for column carrier gas.

d. Hewlett Packard 5970B Mass Selective Detector with RTE-A operating system.

e. Liquid nitrogen dewar for subambient GC oven cooling and sample concentrator.

3. Sample concentration.

a. PACE utilizes a Nutech Model 3521 sample concentrator equipped with appropriate electronic mass flow controllers, valves, and pump along with a Nafion (TM) dryer for moisture control.

b. The Nutech contains a sample trap consisting of 0.32 cm outside diameter nickel tubing loop packed with 60-80 mesh Pyrex beads with glass wool plugs at each end. The nickel tubing loop is wound onto a cylindrically formed tube heater (250 watt). A cartridge heater (25 watt) is sandwiched between pieces of aluminum plate at the trap inlet and outlet to provide additional heat to eliminate cold spots in the transfer tubing. During operation, the trap is inside a two-section stainless steel shell which is well insulated. Rapid heating (-150° C to 180° C in 60 s) is accomplished by direct thermal contact between the heater and the trap tubing. Cooling is achieved by vaporization of liquid nitrogen. In the shell, efficient cooling to -150° C is facilitated by confining the vaporized cryogen to the small open volume surrounding the trap assembly.

c. Two electronic mass flow controllers (MFC) are utilized to maintain constant flow and trap pressure for each run. The first MFC (MFC #1) is in line after the three way valve and before the sample trap. A second MFC (MFC #2) is located in line after the sample trap but before the sample pump. A pressure release vent is placed between MFC #1 and the sample trap. MFC #1 is set 1.5 times greater than MFC #2. MFC #2 controls the flow rate through the sample trap and is usually set at 40 cc/min.

d. The sample canister and internal standard canister are connected to MFC #1 via a three way stainless steel valve. This valve is manually switched to allow for collection of internal standard on the cryo-trap followed by collecting sample or standard.

C. STANDARD CANISTER PREPARATION USING FLASH EVAPORATION

Standard preparation is accomplished by injecting an aliquot of liquid standard, usually in methanol, into a heated zone which is swept with humidified zero grade air. A 1/4" x 10" piece of SUMMA(TM) passivated tubing is wrapped with heat tape and fitted with Swagelock(TM) fittings. One end is equipped with a tee for a capped septum through which the liquid standard is added, and the other end attaches directly to an evacuated 6 L SUMMA(TM) canister. Using a controller, the flash evaporator is heated to 180°C and maintained at this temperature for the duration. An electronic mass flow controller (0-1 SLPM) regulates the flow of air through the evaporator and is placed in line before the 25 mL sparge vessel containing UV treated water for humidification. Based on the air flow rate, usually 1000 mL/min, a final canister volume and concentration is attained. The units of concentration in the final standard canister are ug/m^3.

> For example, if 25 uL of a standard mix containing all target compounds in methanol @ 2 μg/mL is flash evaporated into a final canister volume of 10 L, the final concentration is 500 μg/m^3 or approximately 100 ppbv.

Final standard canister concentration in ppbv corrects for the molar gas volume and percent humidity. A spreadsheet is used to aid in standard preparation amounts to be flash evaporated (see Table 2 for an example of this spreadsheet). All standard preparation is recorded in a standard preparation log book and assigned a standard number.

D. INSTRUMENT OPERATING CONDITIONS

1. Gas chromatograph temperature program:

Initial temp:	-25°C for 1.0 min.
Ramp A:	12°C/min to 50°C
Ramp B:	6°C/min to 140°C
Ramp C:	10°C/min to 190°C, hold 2 min.
Total run time:	28 min.
Carrier flow:	10 mL/min helium

2. Mass spectrometer parameters:

Electron volts:	70 nominal

Scan range: 35 to 300 amu
Scan time: To give at least 5 scans per peak, not to exceed 1 second per scan.
Jet separator temp: 160°C
Interface temp: 190°C

3. The GC/MS system must be set up to meet manufacturer's specification. The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check standard p-bromofluorobenzene (BFB). A BFB standard canister is prepared as in Section VI.C at 1.0 mg/m^3 which results in a final on column amount of 50 ng of BFB when a 50 cc of standard is trapped. The mass spectrum of BFB must be acquired in the following manner. Three scans, the peak apex and the scans immediately preceding and following the apex, are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan prior to the elution of BFB. The instrument performance check (BFB) must meet the ion abundance criteria given in Table 3. The BFB 50 ng tune must be analyzed every 12 hours during sample or standard analysis.

4. Nutech Model 3521 sample concentrator temperatures.
   a. Sample cryogenic trap: trap @ -150°C, desorb @ 180°C
   b. Sample transfer line: 150°C
   c. Instrument transfer line: 150°C

5. Electronic mass flow controller settings.
   a. MFC #1: 60 cc/min
   b. MFC #2: 40 cc/min

6. Nafion (TM) dryer settings.
   a. Dry zero grade air flow: 120 cc/min
   b. Sample collection temperature: 20° C
   c. Reconditioning temperature: 80° C for 10 min.

7. All sample and internal standard lines are of chromatographic grade stainless steel.

E. INTERNAL STANDARD CALIBRATION PROCEDURE

1. Prepare calibration standards at a minimum of three levels as described in Section VI.C for the target compound list. Standard canisters may be stored up to thirty days.

2. Prepare an internal standard canister containing fluorobenzene and p-bromofluorobenzene (BFB) at a concentration equivalent to the midpoint of the calibration. (Note: If interferences exist with the two internal standards listed, alternate compounds may be used which are similar to the target compounds.)

3. Once it has been demonstrated that the GC/MS system meets BFB tune criteria, analyze each calibration standard canister along with the internal standard as described in Section VI.F.

4. Tabulate the area response of the primary ion (Table 4) and the corresponding concentration for each compound and internal standard. Calculate the relative response factors (RRF) for each compound using the following equation:

$$RRF = \frac{(Ax)}{(Ais)} \times \frac{(Cis)}{(Cx)}$$

where,

RRF = relative response factor,
Ax = area of the primary ion for the compound to be measured,
Ais = area of the primary ion for the internal standard,
Cis = concentration of the internal standard (ug/m^3),
Cx = concentration of the compound to be measured (ug/m^3).

The RRF for each compound is calculated using the specific internal standard associated with the compound of interest (see Table 5).

5. The average RRF is calculated for each compound in the calibration , and the % Relative Standard Deviation (% RSD) is calculated based on the RRF values over the working range of the initial calibration curve. The % RSD must be equal to or less than 30% for each compound. Up to 10% of the targets in the compound list can exceed this 30% RSD criteria, however, no compound can exceed 40% RSD. If a compound exceeds 40% RSD, corrective action must be taken such as reanalyzing a standard or preparing a new standard canister.

6. A continuing calibration standard must be analyzed every 12 hours during sam analysis to check the initial calibration curve. The midlevel standard is analyzed after

the GC/MS system meets BFB tune criteria, and the RRF value is calculated for each compound. The % difference of the check standard compared to the average RRF from the initial calibration curve is calculated where,

$$\%D = [(RRFi - RRFc) \times (100)]/(RRFi)$$

where,

RRFi = average RRF from initial curve
RRFc = RRF for compound from check standard

The %D must be within 30% to proceed. Again, 10% of the targets can exceed criteria but must be less than 40% D. If criteria are not met, action must be taken such as reanalysis of the standard or an initial calibration.

7. Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard shifts by more than 0.5 minutes from the latest calibration check, the system must be inspected for malfunctions and appropriate corrections made. The selected ion current profile (SICP) of each internal standard is monitored. If the SICP area changes by more than 50% from the latest calibration check, the system must be inspected and changes made if necessary.

8. If time remains in the 12 hour period after calibration, a calibration check does not need to be analyzed. However, a method blank of humidified zero grade must be analyzed and compliant before samples can be analyzed. A method blank is compliant if no target analytes are found above the MDL. Quantitation is done using the standard which is equivalent to the level of the continuing calibration standard.

9. For each 12 hour period, a system performance check (BFB), continuing calibration standard, and method blank must meet criteria before any sample analysis can begin.

F. SAMPLE ANALYSIS

1. Upon receipt of the sample canister in the analytical lab, the canister pressure (psig) is recorded on the sample tag and in the instrument run log. Any discrepancies are noted concerning sample canister condition. If a canister is received with a vacuum greater than 5" Hg, zero grade is added to the canister to a final pressure of 2-5 psig. A dilution factor will be applied to the analytical results for any sample canisters requiring pressurization as follows:

   Dilution factor (DF) = Ya/Xa

   where,

   Xa = Canister pressure absolute before dilution, and
   Ya = Canister pressure absolute after dilution.
   (Xa and Ya must be in the same units.)

2. Turn sample pump on.
3. Set MFC #1 to 60 cc/min and MFC #2 to 40 cc/min.
4. Set the Nafion (TM) dryer to 20°C.
5. Put the six port valve in the vent mode.
6. Connect the internal standard canister and sample canister to the three way valve.
7. Cool the sample trap to -150°C.
8. Turn the three way valve to the internal standard canister position, and open both the internal standard and sample canister.
9. Turn the six port valve to the trap mode and collect the internal standard for 1 min 4 sec.
10. After the 1 min 4 sec internal standard collection, immediately turn the three way valve to the sample position and collect for 12 min 30 sec.
    Note: The pressure release vent between MFC #1 and the trap should be left open if the canister pressure is >3 psig and closed if <3 psig.
11. While collecting sample, initialize the GCMS system to acquire.
12. Immediately after the 12 min 30 sec of sample collection expires, do the following simultaneously:
    a. Turn the six port valve to vent.
    b. Heat the sample trap to 180° C.
    c. Engage the remote GCMS start button.

13. Close and disconnect the sample canister leaving the three way valve in the sample position. Connect the sample inlet to a source of zero grade air to purge the system between runs..
14. Set the Nafion (TM) dryer to 80° C and recondition for 10 min.
15. If the on-column concentration of any compound exceeds the upper calibration of the instrument, a dilution must be performed. It has been shown that the largest dilution that can be accomplished using this method is a 1:2 dilution. A 250 cc sample volume is trapped as opposed to 500 cc. Sample collection time is adjusted accordingly to 6 min 15 sec @ 40 cc/min. If this dilution is not great enough, the sample may require analysis by gas loop concentration (PACE SOP No. MN-O-457-AH).

G. QUALITATIVE ANALYSIS

1. The compounds listed in Table 1 are identified by an analyst competent in the interpretation of mass spectra. Sample mass spectrum are compared to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the target compound identifications: (1) elution of the sample component at the same GC retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

2. Relative retention time (RRT) of the sample component must agree within +/- 0.06 RRT units of the RRT of the standard component using the continuing check standard as reference.

3. Standard and sample mass spectra are compared using reference spectra obtained on the GC/MS system being used. The mass spectra used for comparison are from the same standard as that being used for RRT comparison. Mass spectral requirements are as follows:

   a. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

   b. The relative intensities of ions specified in 3a. above must agree within +/- 20% between the standard and sample spectra.

   c. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The

verification process should favor false positive.

4. Non-target sample components shall be library searched using the latest NIST library for the purpose of tentative identification. These components are referred to as TICs (Tentatively Identified Compounds) and will be noted as such in any final report with a qualifier of "N". Guidelines for identification are as follows:

   a. Characteristic ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample.

   b. The relative intensities of the major ions should agree within +/- 20%.

   c. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for background contamination or presence of coeluting peaks.

   d. If in the technical judgement of the analyst, no valid identification can be made, the compound will be reported as an unknown with possible classification such as hydrocarbon.

H. QUANTITATIVE ANALYSIS

1. Identified target analytes shall be quantitated using the internal standard method using the SICP area of the characteristic ions of analytes listed in Table 5.

2. The RRF from the continuing calibration standard analysis is used to quantitate samples and blanks. Calculate the concentration of the sample component using the following equation:

$$Xa = [(Ax)(Is)(DF)]/[(Ais)(RRF)]$$

where,

Xa = Target compound air concentration, $\mu g/m^3$,
Ax = Area of the characteristic ion for the compound to be measured,
Ais = Area of the characteristic ion for the specific internal standard,
Is = Amount of internal standard present in $\mu g/m^3$,

RRF = Relative response factor from the analysis of the continuing check standard,

DF = Dilution factor calculated as described in Section VI.F.1. If no dilution is performed, DF equals 1.

Note: To convert $\mu g/m^3$ to ppbv, multiply the $\mu g/m^3$ amount by(24.05606/MW). e.g. 100 $\mu g/m^3$ of trichloroethene is equivalent to 18 ppbv: [(100 $\mu g/m^3$)(24.05606/131.39)]=18 ppbv

3. The internal standard method of quantitation is also used to determine an estimated concentration for TICs. If the nearest internal standard exhibits interferences, the next closest internal is used. Estimated concentration is obtained using the equation in Section VI.H.2. above with the following exceptions:

Ax = Total ion chromatogram area of the TIC,
Ais = Total ion chromatogram area of the specific internal standard,

and the RRF is assumed to be 1.0.

Estimated TIC concentrations will be flagged with a qualifier of "J".

VII. QUALITY CONTROL

A. Three performance criteria are used to demonstrate method validity which are as follows: (1) method detection limit (MDL), (2) replicate precision, and (3) second vendor standard source.

1. MDL is determined following the guidelines set forth in 40CFR136 Appendix B. Seven standard replicates are analyzed at a concentration five times the expected detection limit. The standard deviation is calculated for the seven replicates and this value is multiplied times the Student's t value for 99% confidence. Instrument detection limits are listed in Table 1 based on a 10 cc gas loop.

2. Replicate precision is based upon the relative difference between replicate measurements of the same sample expressed as a percentage,
i.e. [(Measurement #1 - Measurement #2)x100%]/Average of 2 measurements

Replicate calibration standards at 5 five times the expected MDL should be used. A goal of 25% for each compound is based on the EPA CLP SOW No. XXX - Ambient Air February 1991. Table 6 lists replicate precision data.

3. A standard canister is prepared at the midpoint of the calibration using a second vendor source and analyzed to determine accuracy. Agreement within +/- 30% is acceptable where:

$$\text{Accuracy \%} = \frac{\text{(Spiked value - observed value)}}{\text{Spiked value}} \times 100$$

B. Duplicate sample analysis is performed once per 20 samples.

TABLE 1

TARGET COMPOUND LIST

Compound	CAS RN	MDL, ppbv	Expected Retention Time (min.)
DICHLORODIFLUOROMETHANE	75-71-8	2.00	0.871
CHLOROMETHANE	74-87-3	4.80	1.400
FREON 114	1300-37-2	1.40	1.400
VINYL CHLORIDE	75-01-4	3.90	1.741
BROMOMETHANE	74-83-9	2.50	2.475
CHLOROETHANE	75-00-3	3.70	2.816
TRICHLOROFLUOROMETHANE	75-35-4	1.80	4.113
1,1-DICHLOROETHENE	76-13-1	2.50	4.319
TRICHLOROTRIFLUOROETHANE	76-13-1	1.30	4.319
METHYLENE CHLORIDE	75-0902	5.30	4.865
1,1-DICHLOROETHANE	75-34-5	6.00	5.599
cis-1,2-DICHLOROETHENE	156-59-2	4.60	6.196
CHLOROFORM	67-66-3	2.00	6.572
1,1,1-TRICHLOROETHANE	71-55-6	1.80	6.589
CARBON TETRACHLORIDE	56-23-5	1.60	6.743
cis-1,3-DICHLOROPROPENE	10061-01-5	2.60	6.760
BENZENE	71-43-2	3.10	6.931
1,2-DICHLOROETHANE	107-06-2	2.40	7.000
TRICHLOROETHENE	79-01-6	1.80	7.580
1,2-DICHLOROPROPANE	78-87-5	2.10	7.751
TOLUENE	108-88-3	3.40	8.776
trans-1,3-DICHLOROPROPENE	10061-02-6	3.30	9.083
1,1,2-TRICHLOROETHANE	79-06-5	2.60	9.083
TETRACHLOROETHENE	127-18-4	2.10	9.220
1,2-DIBROMOETHANE	106-93-4	1.70	9.579
CHLOROBENZENE	108-90-7	3.00	10.108
ETHYL BENZENE	100-41-4	2.70	10.296
m,p-XYLENE	1330-20-7	6.30	10.416

TABLE 1

TARGET COMPOUND LIST (continued)

Compound	CAS RN	MDL, ppbv	Expected Retention Time (min.)
1,3,5-TRIMETHYLBENZENE	108-42-5	2.30	11.219
1,1,2,2-TETRACHLOROETHANE	79-43-5	1.80	11.612
1,2,4-TRIMETHYLBENZENE	95-63-6	2.60	11.920
1,3-DICHLOROBENZENE	541-73-1	1.90	12.587
1,4-DICHLOROBENZENE	106-46-7	2.20	12.707
BENZYL CHLORIDE	100-44-7	3.40	12.929
1,2-DICHLOROBENZENE	95-50-1	2.00	13.151
1,2,4-TRICHLOROBENZENE	120-82-1	2.20	15.508
HEXACHLOROBUTADIENE	87-68-3	0.92	15.901

TABLE 2

STD SPREADSHEET

VOCCS Gas Standard Preparation Worksheet

Dry volume of zero air added to canister: 20
Reference temp. of mass flow controller (°F): 70
Dilution solvent density: 0.7913 (Methanol)
Dilution solvent mole. wt.: 32.04 (Methanol)
Total volume of solution added: 2

Gas Moisture Content Specifications

Compound No. From Table	Compound Name	Molecular Weight	Liquid Density g/ml	Desired Moisture %, v/v	Water Required µl (liq.)	Actual Water µl (liq.)	True Moisture %, v/v
0	Water, High Purity	18.015	0.9982			200	1.32

VOC Standards Specifications for Stock Solutions

Compound No. From Table	Compound Name (verify)	Molecular Weight	Stock Solution Concen. µg/ml	Desired Conc. PPM, v/v	Volume Solution Required µl	Actual Volume Solution µl	True Conc. of Standard PPM, v/v
1	Benzene [a] [b]	78.11	20000.0			50.0	15.243
2	Benzyl Chloride [a] [b]	126.58	20000.0			50.0	9.406
3	Bromomethane	94.95	20000.0			50.0	12.539
4	Carbon Tetrachloride [a] [b]	153.84	20000.0			50.0	7.739
5	Chlorobenzene [a] [b]	112.56	20000.0			50.0	10.578
6	Chloroethane	64.52	20000.0			50.0	18.453
7	Chloroform [a] [b]	119.39	20000.0			50.0	9.972
8	Chloromethane	50.49	20000.0			50.0	23.581
9	1,2-Dibromoethane [a]	187.88	20000.0			50.0	6.337
10	m-Dichlorobenzene [a] [b]	147.01	20000.0			50.0	8.099
11	o-Dichlorobenzene [a] [b]	147.01	20000.0			50.0	8.099
12	p-Dichlorobenzene [a] [b]	147.01	20000.0			50.0	8.099
13	Dichlorodifluoromethane [a]	120.92	20000.0			50.0	9.846
14	1,1-Dichloroethane [a]	98.97	20000.0			50.0	12.030
15	1,2-Dichloroethane [a]	98.96	20000.0			50.0	12.031
16	1,1-Dichloroethene	96.95	20000.0			50.0	12.281
17	cis-1,2-Dichloroethylene [a]	96.95	20000.0			50.0	12.281
18	1,2-Dichloropropane [a]	112.99	20000.0			50.0	10.537
19	cis-1,3-Dichloropropene [a] [b]	110.98	20000.0			50.0	10.726
20	trans-1,3-Dichloropropens [a] [b]	110.98	20000.0			50.0	10.726
21	1,2-Dichloro-1,1,2,2-tetrafluoroethane	170.93	20000.0			50.0	6.965
22	Ethylbenzene [a] [b]	106.16	20000.0			50.0	11.215
23	Hexachloro-1,3-butadiene [a]	260.76	20000.0			50.0	4.566
24	Methylene Chloride [a]	84.94	20000.0			50.0	14.017
25	Styrene [a] [b]	104.14	20000.0			50.0	11.433
26	1,1,2,2-Tetrachloroethane [a]	167.86	20000.0			50.0	7.093
27	Tetrachloroethylene [a] [b]	165.85	20000.0			50.0	7.179
28	Toluene [a] [b]	92.13	20000.0			50.0	12.923
29	1,2,4-Trichlorobenzene [a] [b]	181.46	20000.0			50.0	6.561
30	1,1,1-Trichloroethane [a]	133.42	20000.0			50.0	8.924
31	1,1,2-Trichloroethane [a] [b]	133.42	20000.0			50.0	8.924
32	Trichloroethene	131.4	20000.0			50.0	9.061
33	Trichlorofluoromethane [a]	137.38	20000.0			50.0	8.667
34	1,1,2-Trichloro-1,2,2-trifluoroethane [a]	187.38	20000.0			50.0	6.354
35	1,2,4-Trimethylbenzene [a]	120.19	20000.0			50.0	9.906
36	1,3,5-Trimethylbenzene [a]	120.19	20000.0			50.0	9.906
37	Vinyl Chloride [a] [b]	62.5	20000.0			50.0	19.050
38	m-Xylene [a] [b]	106.16	20000.0			50.0	11.215
39	o-Xylene [a] [b]	106.16	20000.0			50.0	11.215
40	p-Xylene [a] [b]						

TABLE 3

REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95 (See note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4

CHARACTERISTIC IONS FOR TARGET COMPOUNDS

Parameter	Primary Ion*	Secondary Ion(s)
Vinyl chloride	62	27, 64
Trichloroethene	130	132, 95
Chloroform	83	85, 47
Benzene	78	77, 50
Carbon tetrachloride	117	119
Tetrachloroethene	164	129, 131, 166
1-dichloroethene	61	96, 63
1,2-dichloroethane	62	27, 64
Chlorobenzene	112	77, 114
1,1,1-trichloroethane	97	99, 61
1,1,2-trichloroethane	97	83, 61
1,1,2,2-tetrachloroethane	83	85
Ethyl benzene	91	106
Methylene chloride	49	84, 86
1,2,4-trichlorobenzene	180	182, 184
Styrene	104	78, 103
1,1-dichloroethane	63	27, 65
Toluene	91	92
Xylenes, o-, m-, and p-	91	106
1,2-dichloropropane	63	41, 62
1,2-dichlorobenzene	146	148, 111
1,2-dibromoethane	107	109, 27
Chloroethane	64	29, 27
Benzyl chloride	91	126
cis-1,3-dichloropropene	75	39, 77

* The primary ion should be used unless interferences are present, in which case a secondary ion may be used.

TABLE 4 (continued)

CHARACTERISTIC IONS FOR TARGET COMPOUNDS

Parameter	Primary Ion*	Secondary Ion(s)
trans-1,2-dichloroethene	61	96, 98
1,4-dichlorobenzene	146	148, 111
Hexachlorobutadiene	225	227, 223
Bromomethane	94	96
trans-1,3-dichloropropene	75	39, 77
Dichlorodifluoromethane	85	87
Chloromethane	50	52
cis-1,2-dichloroethene	61	96, 98
1,3-dichlorobenzene	146	148, 111
1,1,2-trichloro-1,2,2-trifluoroethane	151	101, 103
Trichlorofluoromethane	101	103
1,2-dichloro-1,1,2,2-tetrafluoroethane	85	135, 87
1,3,5-trimethylbenzene	105	120
1,2,4-trimethylbenzene	105	120

* The primary ion should be used unless interferences are present, in which case a secondary ion may be used.

TABLE 5

INTERNAL STANDARDS AND ASSOCIATED COMPOUNDS

Fluorobenzene (IS #1)	Bromofluorobenzene (IS #2)
Dichlorodifluoromethane	1,1,2-Trichloroethane
Chloromethane	Tetrachloroethene
Freon 114	1,2-Dibromoethane
Vinyl chloride	Chlorobenzene
Bromomethane	Ethyl benzene
Chloroethane	m,p-Xylene
Trichlorofluoromethane	o-Xylene
1,1-Dichloroethene	Styrene
Trichlorotrifluoroethane	1,3,5-Trimethylbenzene
Methylene chloride	1,1,2,2-Tetrachloroethane
1,1-Dichloroethane	1,2,4-Trimethylbenzene
cis-1,2-Dichloroethene	1,3-Dichlorobenzene
Chloroform	1,4-Dichlorobenzene
1,1,1-Trichloroethane	Benzyl chloride
Carbon tetrachloride	1,2-Dichlorobenzene
cis-1,3-Dichloropropene	1,2,4-Trichlorobenzene
Benzene	Hexachlorobutadiene
1,2-Dichloroethane	
Trichloroethene	
1,2-Dichloropropane	
Toluene	
trans-1,3-Dichloropropene	

TABLE 6

REPLICATE PRECISION

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COPY #9

STANDARD OPERATING PROCEDURE

MODIFIED EPA COMPENDIUM METHOD TO-14 FOR ANALYSIS OF HIGH LEVEL (PPMV) VOLATILE ORGANIC COMPOUNDS IN AIR USING SUMMA(TM) PASSIVATED CANISTERS BY GAS LOOP INJECTION AND GAS CHROMATOGRAPHY/MASS SPECTROSCOPY (GCMS)

SOP NUMBER	MN-0-457-AH
AUTHOR	Steve Sanders
EFFECTIVE DATE	May 25, 1993
SUPERSEDES	First Issue

APPROVALS

Air Analytical Supervisor — Date: 05/28/93

Manager Air Analytical — Date: 5/28/93

Quality Assurance Officer — Date: 5/28/93

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I. PURPOSE

The purpose of this Standard Operating Procedure is to provide quality control and analytical guidance for the analysis of whole air samples contained in SUMMA (TM) passivated canisters using gas chromatography/mass spectrometry. A laboratory designed gas loop sample concentrator is utilized to transport the sample onto the GC column.

II. SCOPE/APPLICATION

A. SCOPE

This modified EPA Method TO-14 is designed to encompass air samples not applicable to Compendium Method TO-14. The compendium method has an instrument working linear range of 1 part per billion by volume (ppbv) to 100 ppbv designed for ambient air samples. Source level or part per million by volume (ppvm) level samples are analyzed by GCMS utilizing a gas loop concentrator to reduce on-column sample amount. Compendium method TO-14 cryo-traps a 400 to 500 cc sample on a trap packed with glass beads. The trap is then heated and desorbed onto the analytical column for separation followed by mass spectroscopy detection in the full scan mode. Gas loop reduces the amount of samples loaded onto the column decreasing the likelihood of detector saturation when dealing with source level whole air samples such as stack, soil vapor, and landfill samples containing ppmv levels of contaminants. Gas loop sizes range from 0.010 cc to 10 cc which allows for a working range of 0.10 ppmv to 10,000 ppmv. Sample canisters, transfer lines, and the ten port valve containing the sample loop are all heated to reduce carryover and ensure sample vaporization within the canister. Target compounds applicable to this method are listed in Table 1.

B. SAFETY

The toxicity of carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. A current awareness file of OSHA regulations regarding the safe handling of the chemicals specified and a reference file of material safety data sheets is maintained in the laboratory and is available to all personnel involved in the chemical analysis.

III. RESPONSIBILITY

A. QUALITY ASSURANCE OFFICER

1. The Quality Assurance Officer has overall responsibility for monitoring implementation of and adherence to the policies and procedures set forth in this document.

2. The Quality Assurance Officer will conduct semiannual audits of the facility to monitor adherence to this and other SOPs. The results of the audit will be reported to Regional Management and Corporate Quality.

B. ORGANIC LABORATORY MANAGER/SECTION SUPERVISOR

1. The manager/supervisor is responsible for ensuring adherence to this SOP.

2. The manager/supervisor will ensure that this SOP is reviewed on an annual basis.

3. The manager/supervisor will ensure that the Quality Assurance Officer is notified when revisions to the SOP are required.

C. ANALYST

1. The analyst is responsible for following all procedures set forth in this document. The analyst will report any deviations to the procedures set forth in this document.

2. The analyst is responsible for reviewing the SOP on an annual basis and reporting any required revisions to the department manager or supervisor.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.

B. At the time of review, any required revisions will be incorporated and the superseded document replaced.

V. DISTRIBUTION

A. Distribution of this SOP will be determined by the Quality Assurance Officer.

B. Distribution records will be maintained by the Quality Assurance Officer.

VI. PROCEDURE

A. DEFINITIONS

1. Absolute canister pressure = Pg + Pa, where Pg = gauge pressure in the canister (kPa, psig) and Pa = barometric pressure.

2. Absolute pressure - Pressure measured with reference to absolute zero as opposed to atmospheric pressure, usually expressed as kPa, mm Hg or psia.

3. Cryogen - A refrigerant used to obtain very low temperatures in the gas chromatographic oven. A typical cryogen is liquid nitrogen (bp - 195.8°C).

4. Dynamic calibration - Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

5. Gauge pressure - Pressure measured above ambient atmospheric pressure as opposed to absolute pressure. Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

6. MS-SCAN - The GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run. As used in the current context, this procedure serves a qualitative identification and characterization of the sample.

7. Megabore(TM) column - Chromatographic column having an internal diameter (I.D.) greater than 0.50 mm. The Megabore(TM) column is a trademark of the J&W Scientific Co. For purposes of this SOP, Megabore(TM) refers to chromatographic columns with 0.53 mm I.D.

8. Qualitative accuracy - The ability of an analytical system to correctly identify compounds.

9. Quantitative accuracy - The ability of an analytical system to correctly, measure the concentration of an identified compound.

B. MATERIALS, SUPPLIES, AND EQUIPMENT NEEDED

1. Standard preparation materials.

   a. 10, 25, 50, 100, 250, 500; and 1000 uL gas tight syringes (Hamilton).

   b. Supelco custom standard mixes in methanol at 20 mg/mL and Chem Serv individual neat standards or equivalent.

   c. Burdick and Jackson purge and trap grade methanol.

   d. Various sizes of class A glass volumetric flasks.

   e. SUMMA(TM) passivated canisters, six liter capacity and 40 spig maximum pressure.

   f. Zero grade air high pressure cylinder.

   g. 0-1 SLPM electronic mass flow controller with controller.

   h. 25 mL sparge vessel for humidification purposes.

   i. Laboratory designed flash evaporator consisting of a 1/4" x 10" stainless steel SUMMA(TM) passivated tubing wrapped with heat wrap. One end is fitted with a Swagelock(TM) tee for a zero grade inlet and septum cap. The other end fits directly onto the canister.

   j. Heat controller capable of heating and maintaining a temperature of 180°C.

   k. Electronic flow meter to aid in setting the zero grade air flow at 1000 mL/min.

2. Analytical instrumentation.

   a. Hewlett Packard 5890 Series II gas chromatograph with make up gas for an SGE glass jet separator.

   b. J & W Scientific DB-624 30m x 0.53mm Megabore(TM) column.

   c. Chromatographic grade high pressure helium cylinder for column carrier gas.

   d. Hewlett Packard 5971A mass selective detector with UNIX/Target operating system.

   e. Liquid nitrogen dewar for subambient GC oven cooling.

3. Sample concentration.

   a. Laboratory designed gas loop sample concentrator equipped with a 10 port Valco(TM) valve in a heated zone which can be equipped with two sample loops - one for internal standard addition and one for sample concentration. Heated transfer lines connecting the concentrator to the sample oven and gas chromatograph. A manual switch to turn the valve from the sample collection to sample desorb. A stainless steel pump is used to draw the air sample through the sample gas loop. All sampling handling lines are of chromatographic grade stainless steel.

   b. Sample gas loops: 0.010, 0.050, 0.100, 0.250, 0.500, 1.0, 2.0, 5.0, and 10 cc sizes.

   c. Despatch LDB Series oven for heating sample and standard canisters with capacity for two 6 L canisters.

C. STANDARD CANISTER PREPARATION USING FLASH EVAPORATION

Standard preparation is accomplished by injecting an aliquot of liquid standard, usually in methanol, into a heated zone which is swept with humidified zero grade air. A 1/4" x 10" piece of SUMMA(TM) passivated tubing is wrapped with heat tape and fitted with Swagelock(TM) fittings. One end is equipped with a tee for a capped septum through

which the liquid standard is added, and the other end attaches directly to an evacuated 6 L SUMMA(TM) canister. Using a controller, the flash evaporator is heated to 180°C and maintained at this temperature for the duration. An electronic mass flow controller (0-1 SLPM) regulates the flow of air through the evaporator and is placed in line before the 25 mL sparge vessel containing UV treated water for humidification. Based on the air flow rate, usually 1000 mL/min, a final canister volume and concentration is attained. The units of concentration in the final standard canister are ppmv or mg/m^3.

> For example, if 5.0 uL of a neat solution of 1,2-dichloroethane is added to a canister containing 15 L of air, the final concentration is 100 ppmv.

Final standard canister concentration corrects for the molar gas volume and percent humidity. A spreadsheet is used to aid in standard preparation amounts to be flash evaporated (see Table 2 for an example of this spreadsheet). All standard preparation is recorded in a standard preparation log book and assigned a standard number.

D. INSTRUMENT OPERATING CONDITIONS

1. Gas chromatograph temperature program:

Initial temp:	-50°C for 0.25 min.
Ramp A:	12°C/min to 80°C
Ramp B:	8°C/min to 150°C
Ramp C:	30°C/min to 200°C, hold 2 min.
Total run time:	24.50 min.
Carrier flow:	10 mL/min helium
Make up gas:	20 mL/min helium

2. Mass spectrometer parameters:

Electron volts:	70 nominal
Scan range:	35 to 300 amu
Scan time:	To give at least 5 scans per peak, not to exceed 1 second per scan.
Jet separator temp:	200°C
Interface temp:	250°C

3. The GC/MS system must be set up to meet manufacturer's specification. The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check standard p-bromofluorobenzene (BFB). A BFB standard canister is prepared as in Section VI.C at 100 mg/m^3 which results in a final on column amount of 50 ng of BFB when a 0.500 cc loop is used. The mass spectrum of BFB must be acquired in the following manner. Three scans, the peak apex and the scans immediately preceding and following the apex, are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan prior to the elution of BFB. The instrument performance check (BFB) must meet the ion abundance criteria given in Table 3. The BFB 50 ng tune must be analyzed every 12 hours during sample or standard analyses.

4. Gas loop sample concentrator temperatures.

Sample oven:	150°C
Sample transfer line:	175°C
Gas loop oven and valve:	150°C
Instrument transfer line:	175°C

   a. Sample loop sizes will vary from 0.010 cc to 10 cc depending on sample concentration range.

   b. Internal standard loop size will be 0.500 cc.

5. All sample and internal standard lines are chromatographic grade stainless steel and are heated.

E. INTERNAL STANDARD CALIBRATION PROCEDURE

1. Prepare calibration standards at a minimum of three levels as described in Section VI.C for the target compound list. Standard canisters may be stored up to thirty days.

2. Prepare an internal standard canister containing fluorobenzene and p-bromofluorobenzene (BFB) at a concentration equivalent to the midpoint of the calibration. (Note: If interferences exist with the two internal standards listed,

alternate compounds may be used which are similar to the target compounds.)

3. Once it has been demonstrated that the GC/MS system meets BFB tune criteria, analyze each calibration standard canister along with the internal standard as described in Section VI.F.

4. Tabulate the area response of the primary ion (Table 4) and the corresponding concentration for each compound and internal standard. Calculate the relative response factors (RRF) for each compound using the following equation:

$$RRF = (Ax/Ais)/(Cis/Cx)$$

where,

RRF	=	relative response factor,
Ax	=	area of the primary ion for the compound to be measured,
Ais	=	area of the primary ion for the internal standard,
Cis	=	concentration of the internal standard (ppmv),
Cx	=	concentration of the compound to be measured (ppmv).

The RRF for each compound is calculated using the specific internal standard associated with the compound of interest (see Table 5).

5. The average RRF is calculated for each compound in the calibration , and the % Relative Standard Deviation (% RSD) is calculated based on the RRF values over the working range of the initial calibration curve. The % RSD must be equal to or less than 30% for each compound. Up to 10% of the targets in the compound list can exceed this 30% RSD criteria, however, no compound can exceed 40% RSD. If a compound exceeds 40% RSD, corrective action must be taken such as reanalyzing a standard or preparing a new standard canister.

6. A calibration check standard must be analyzed every 12 hours during sample analysis to check the initial calibration curve. The midlevel standard is analyzed after the GC/MS system meets BFB tune criteria, and the RRF value is calculated for each compound. The % difference of the check standard compared to the average RRF from the initial calibration curve is calculated where,

$$\%D = [(RRFi - RRFc)\ (100)]/(RRFi)$$

where,

RRFi = average RRF from initial curve
RRFc = RRF for compound from check standard

The %D must be within 30% to proceed. Again, 10% of the targets can exceed criteria but must be less than 40% D. If criteria are not met, action must be taken such as reanalysis of the standard or an initial calibration.

7. Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard shifts by more than 0.5 minutes from the latest calibration check, the system must be inspected for malfunctions and appropriate corrections made. The selected ion current profile (SICP) of each internal standard is monitored.

   If the SICP area changes by more than 50% from the latest calibration check, the system must be inspected and changes made if necessary.

8. If time remains in the 12 hour period after calibration, a calibration check does not need to be analyzed. However, a method blank of humidified zero grade must be analyzed and compliant before samples can be analyzed. A method blank is compliant if no target analytes are found above the MDL. Quantitation is done using the standard which is equivalent to the level of the continuing calibration standard.

9. For each 12 hour period, a system performance check (BFB), continuing calibration, and method blank must meet criteria before any sample analysis can begin.

F. SAMPLE ANALYSIS

1. Upon receipt of the sample canister in the analytical lab, the canister pressure (psig) is recorded on the sample tag and in the instrument run log. Any discrepancies are noted concerning sample canister condition. If a canister is received with a vacuum greater than 5" Hg, zero grade is added to the canister

to a final pressure of 2-5 psig. A dilution factor will be applied to the analytical results for any sample canisters requiring pressurization as follows:

Dilution factor (DF) = Ya/Xa

where,

Xa = Canister pressure absolute before dilution, and
Ya = Canister pressure absolute after dilution.
(Xa and Ya must be in the same units.)

2. The sample canister is placed in an oven at 150°C and allowed to equilibrate for 30 minutes. Two canisters fit in the oven at one time allowing for equilibrium. A heated 1/8" stainless steel sample transfer line is connected to the canister inside the sample oven.

3. Internal standard is added to the internal standard loop through a different port of the valve than the sample in the collection mode. The internal standard canister is kept at positive pressure to facilitate transfer.

4. Once the GC reaches the ready status, the sample pump is turned on followed by opening the sample canister Nupro (TM) valve. The internal standard canister is also opened.

   Note: It is important to first turn the sample pump on before opening the sample canister to eliminate any backflow into the canister. The valve is left in the collection or vent mode for 30 seconds to allow the loops to reach equilibrium. A 0.010 cc loop in-line before the valve is used for both the internal standard and sample lines to maintain constant pressure in the gas loops due to the very small inside diameter of the 0.010 cc loop.

5. After 30 seconds, the valve is manually turned to the inject mode and the remote GC/MS start button is engaged. Column carrier flow sweeps the contents of both loops onto the column for separation followed MS detection. Both canisters are then closed, and the sample canister is disconnected from the transfer line. The sample pump is left on to sweep the transfer line between runs.

6. If the on-column concentration of any compound exceeds the upper calibration, a dilution must be performed to bring the concentration within the calibration range. Dilutions are performed simply by reducing the amount of sample being loaded on the column. This is done by using a smaller gas loop volume. For example, if the sample was analyzed using a 10 cc loop and a 1:100 dilution was required, the 10 cc loop would be replaced with a 0.100 cc gas loop and the sample would be analyzed. Any results obtained from the 1:100 dilution would be multiplied by 100 as would the method detection limit (MDL).

G. QUALITATIVE ANALYSIS

1. The compounds listed in Table 1 are identified by an analyst competent in the interpretation of mass spectra. Sample mass spectrum are compared to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the target compound identifications: (1) elution of the sample component at the same GC retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

2. Relative retention time (RRT) of the sample component must agree within +/- 0.06 RRT units of the RRT of the standard component using the continuing check standard as reference.

3. Standard and sample mass spectra are compared using reference spectra obtained on the GC/MS system being used. The mass spectra used for comparison are from the same standard as that being used for RRT comparison. Mass spectral requirements are as follows:

   a. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

   b. The relative intensities of ions specified in 3a. above must agree within +/- 20% between the standard and sample spectra.

   c. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positive.

4. Non-target sample components shall be library searched using the latest NIST library for the purpose of tentative identification. These components are referred to as TICs (Tentatively Identified Compounds) and will be noted as such in any final report with a qualifier of "N". Guidelines for identification are as follows:

   a. Characteristic ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample.

   b. The relative intensities of the major ions should agree within +/- 20%.

   c. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for background contamination or presence of coeluting peaks.

   d. If in the technical judgement of the analyst, no valid identification can be made, the compound will be reported as an unknown with possible classification such as hydrocarbon.

H. QUANTITATIVE ANALYSIS

1. Identified target analytes shall be quantitated using the internal standard method using the SICP area of the characteristic ions of analytes listed in Table 5.

2. The RRF from the continuing calibration standard analysis is used to quantitate samples and blanks. Calculate the concentration of the sample component using the following equation:

$$Xa = [(Ax)(Is)(DF)]/[(Ais)(RRF)]$$

where,

Xa = Target compound air concentration, ppmv,
Ax = Area of the characteristic ion for the compound to be measured,
Ais = Area of the characteristic ion for the specific internal standard,
Is = Amount of internal standard present in ppmv,

RRF = Relative response factor from the analysis of the continuing check standard,

DF = Dilution factor calculated as described in Section VI.F.1. If no dilution is performed, DF equals 1.

3. The internal standard method of quantitation is also used to determine an estimated concentration for TICs. If the nearest internal standard exhibits interferences, the next closest internal is used. Estimated concentration is obtained using the equation in Section VI.H.2. above with the following exceptions:

Ax = Total ion chromatogram area of the TIC,

Ais = Total ion chromatogram area of the specific internal standard,

and the RRF is assumed to be 1.0.

Estimated TIC concentrations will be flagged with a qualifier of "J".

VII. QUALITY CONTROL

A. Three performance criteria are used to demonstrate method validity which are as follows: (1) method detection limit (MDL), (2) replicate precision, and (3) second vendor standard source.

1. MDL is determined following the guidelines set forth in 40CFR136 Appendix B. Seven standard replicates are analyzed at a concentration five times the expected detection limit. The standard deviation is calculated for the seven replicates and this value is multiplied times the Student's t value for 99% confidence. Instrument detection limits are listed in Table 1 based on a 10 cc gas loop.

2. Replicate precision is based upon the relative difference between replicate measurements of the same sample expressed as a percentage,
i.e. [(Measurement #1 - Measurement #2)x100%]/Average of 2 measurements

Replicate calibration standards at 5 five times the expected MDL should be used. A goal of 25% for each compound is based on the EPA CLP SOW No. XXX - Ambient Air February 1991. Table 6 lists replicate precision data.

3. A standard canister is prepared at the midpoint of the calibration using a second vendor source and analyzed to determine accuracy. Agreement within +/- 30% is acceptable where:

$$\text{Accuracy \%} = \frac{\text{(Spiked value - observed value)}}{\text{Spiked value}} \times 100$$

B. Duplicate sample analysis is performed once per 20 samples.

TABLE 1

TARGET COMPOUND LIST

Compound	CAS RN	MDL, ppmv	Expected Retention Time (min.)
1 DICHLORODIFLUOROMETHANE	75-71-8		0.871
2 CHLOROMETHANE	74-87-3		1.400
3 FREON 114	1300-37-2		1.400
4 VINYL CHLORIDE	75-01-4		1.741
BROMOMETHANE	74-83-9		2.475
CHLOROETHANE	75-00-3		2.816
7 TRICHLOROFLUOROMETHANE	75-35-4		4.113
8 1,1-DICHLOROETHENE	76-13-1		4.319
9 TRICHLOROTRIFLUOROETHANE	76-13-1		4.319
10 METHYLENE CHLORIDE	75-0902		4.865
11 1,1-DICHLOROETHANE	75-34-5		5.599
12 cis-1,2-DICHLOROETHENE	156-59-2		6.196
13 CHLOROFORM	67-66-3		6.572
14 1,1,1-TRICHLOROETHANE	71-55-6		6.589
15 CARBON TETRACHLORIDE	56-23-5		6.743
16 cis-1,3-DICHLOROPROPENE	10061-01-5		6.760
17 BENZENE	71-43-2		6.931
18 1,2-DICHLOROETHANE	107-06-2		7.000
19 TRICHLOROETHENE	79-01-6		7.580
20 1,2-DICHLOROPROPANE	78-87-5		7.751
21 TOLUENE	108-88-3		8.776
22 trans-1,3-DICHLOROPROPENE	10061-02-6		9.083
23 1,1,2-TRICHLOROETHANE	79-06-5		9.083
24 TETRACHLOROETHENE	127-18-4		9.220
25 1,2-DIBROMOETHANE	106-93-4		9.579
26 CHLOROBENZENE	108-90-7		10.108
ETHYL BENZENE	100-41-4		10.296
26 m,p-XYLENE	1330-20-7		10.416

TABLE 1

TARGET COMPOUND LIST (continued)

Compound	CAS RN	MDL, ppmv	Expected Retention Time (min.)
31 1,3,5-TRIMETHYLBENZENE	108-42-5		11.219
32 1,1,2,2-TETRACHLOROETHANE	79-43-5		11.612
33 1,2,4-TRIMETHYLBENZENE	95-63-6		11.920
34 1,3-DICHLOROBENZENE	541-73-1		12.587
35 1,4-DICHLOROBENZENE	106-46-7		12.707
36 BENZYL CHLORIDE	100-44-7		12.929
37 1,2-DICHLOROBENZENE	95-50-1		13.151
38 1,2,4-TRICHLOROBENZENE	120-82-1		15.508
39 HEXACHLOROBUTADIENE	87-68-3		15.901

TABLE 2

STD SPREADSHEET

VOCCS Gas Standard Preparation Worksheet

Dry volume of zero air added to canister: 20
Reference temp. of mass flow controller (°F): 70
Dilution solvent density: 0.7913
Dilution solvent mole. wt.: 32.04
Total volume of solution added: 2

Gas Moisture Content Specifications

Compound No. From Table	Compound Name	Molecular Weight	Liquid Density g/ml	Desired Moisture %, v/v	Water Required µl (liq.)	Actual Water µl (liq.)	True Moisture %, v/v
0	Water, High Purity	18.015	0.9982			200	1.32

VOC Standards Specifications for Stock Solutions

Compound No. From Table	Compound Name (verify)	Molecular Weight	Stock Solution Concen. µg/ml	Desired Conc. PPM, v/v	Volume Solution Required µl	Actual Volume Solution µl	True Conc. of Standard PPM, v/v
1	Benzene [1] [2]	78.11	20000.0			50.0	15.243
2	Benzyl Chloride [1] [2]	126.58	20000.0			50.0	9.406
3	Bromomethane	94.95	20000.0			50.0	12.539
4	Carbon Tetrachloride [1] [2]	153.84	20000.0			50.0	7.739
5	Chlorobenzene [1] [2]	112.56	20000.0			50.0	10.578
6	Chloroethane	64.52	20000.0			50.0	18.453
7	Chloroform [1] [2]	119.39	20000.0			50.0	9.972
8	Chloromethane	50.49	20000.0			50.0	23.581
9	1,2-Dibromoethane [1]	187.88	20000.0			50.0	6.337
10	m-Dichlorobenzene [1] [2]	147.01	20000.0			50.0	8.099
11	o-Dichlorobenzene [1] [2]	147.01	20000.0			50.0	8.099
12	p-Dichlorobenzene [1] [2]	147.01	20000.0			50.0	8.099
13	Dichlorodifluoromethane [1]	120.92	20000.0			50.0	9.846
14	1,1-Dichloroethane [1]	98.97	20000.0			50.0	12.030
15	1,2-Dichloroethane [1]	98.96	20000.0			50.0	12.031
16	1,1-Dichloroethene	96.95	20000.0			50.0	12.281
17	cis-1,2-Dichloroethylene [1]	96.95	20000.0			50.0	12.281
18	1,2-Dichloropropane [1]	112.99	20000.0			50.0	10.537
19	cis-1,3-Dichloropropene [1] [2]	110.98	20000.0			50.0	10.728
20	trans-1,3-Dichloropropene [1] [2]	110.98	20000.0			50.0	10.728
21	1,2-Dichloro-1,1,2,2-tetrafluoroethane	170.93	20000.0			50.0	6.965
22	Ethylbenzene [1] [2]	106.16	20000.0			50.0	11.215
23	Hexachloro-1,3-butadiene [1]	260.76	20000.0			50.0	4.566
24	Methylene Chloride [1]	84.94	20000.0			50.0	14.017
25	Styrene [1] [2]	104.14	20000.0			50.0	11.433
26	1,1,2,2-Tetrachloroethane [1]	167.86	20000.0			50.0	7.093
27	Tetrachloroethylene [1] [2]	165.85	20000.0			50.0	7.179
28	Toluene [1] [2]	92.13	20000.0			50.0	12.923
29	1,2,4-Trichlorobenzene [1] [2]	181.46	20000.0			50.0	6.561
30	1,1,1-Trichloroethane [1]	133.42	20000.0			50.0	8.924
31	1,1,2-Trichloroethane [1] [2]	133.42	20000.0			50.0	8.924
32	Trichloroethene	131.4	20000.0			50.0	9.061
33	Trichlorofluoromethane [1]	137.38	20000.0			50.0	8.667
34	1,1,2-Trichloro-1,2,2-trifluoroethane [1]	187.38	20000.0			50.0	6.354
35	1,2,4-Trimethylbenzene [1]	120.19	20000.0			50.0	9.936
36	1,3,5-Trimethylbenzene [1]	120.19	20000.0			50.0	9.936
37	Vinyl Chloride [1] [2]	62.5	20000.0			50.0	19.050
38	m-Xylene [1] [2]	106.16	20000.0			50.0	11.215
39	o-Xylene [1] [2]	106.16	20000.0			50.0	11.215
40	p-Xylene [1] [2]	106.16	20000.0			50.0	11.215

TABLE 3

REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95 (See note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4

CHARACTERISTIC IONS FOR TARGET COMPOUNDS

Parameter	Primary Ion*	Secondary Ion(s)
Vinyl chloride	62	27, 64
Trichloroethene	130	132, 95
Chloroform	83	85, 47
Benzene	78	77, 50
Carbon tetrachloride	117	119
Tetrachloroethene	164	129, 131, 166
'-dichloroethene	61	96, 63
ı,2-dichloroethane	62	27, 64
Chlorobenzene	112	77, 114
1,1,1-trichloroethane	97	99, 61
1,1,2-trichloroethane	97	83, 61
1,1,2,2-tetrachloroethane	83	85
Ethyl benzene	91	106
Methylene chloride	49	84, 86
1,2,4-trichlorobenzene	180	182, 184
Styrene	104	78, 103
1,1-dichloroethane	63	27, 65
Toluene	91	92
Xylenes, o-, m-, and p-	91	106
1,2-dichloropropane	63	41, 62
1,2-dichlorobenzene	146	148, 111
1,2-dibromoethane	107	109, 27
Chloroethane	64	29, 27
Benzyl chloride	91	126
cis-1,3-dichloropropene	75	39, 77

* The primary ion should be used unless interferences are present, in which case a secondary ion may be used.

TABLE 4 (continued)

CHARACTERISTIC IONS FOR TARGET COMPOUNDS

Parameter	Primary Ion*	Secondary Ion(s)
trans-1,2-dichloroethene	61	96, 98
1,4-dichlorobenzene	146	148, 111
Hexachlorobutadiene	225	227, 223
Bromomethane	94	96
trans-1,3-dichloropropene	75	39, 77
Dichlorodifluoromethane	85	87
Chloromethane	50	52
cis-1,2-dichloroethene	61	96, 98
1,3-dichlorobenzene	146	148, 111
1,1,2-trichloro-1,2,2-trifluoroethane	151	101, 103
Trichlorofluoromethane	101	103
1,2-dichloro-1,1,2,2-tetrafluoroethane	85	135, 87
1,3,5-trimethylbenzene	105	120
1,2,4-trimethylbenzene	105	120

* The primary ion should be used unless interferences are present, in which case a secondary ion may be used.

TABLE 5

INTERNAL STANDARDS AND ASSOCIATED COMPOUNDS

Fluorobenzene (IS #1)	Bromofluorobenzene (IS #2)
Dichlorodifluoromethane	1,1,2-Trichloroethane
Chloromethane	Tetrachloroethene
Freon 114	1,2-Dibromoethane
Vinyl chloide	Chlorobenzene
Bromomethane	Ethyl benzene
Chloroethane	m,p-Xylene
[illegible]chlorofluoromethane	o-Xylene
[illegible]-Dichloroethene	Styrene
Trichlorotrifluoroethane	1,3,5-Trimethylbenzene
Methylene chloride	1,1,2,2-Tetrachloroethane
1,1-Dichloroethane	1,2,4-Trimethylbenzene
cis-1,2-Dichloroethene	1,3-Dichlorobenzene
Chloroform	1,4-Dichlorobenzene
1,1,1-Trichloroethane	Benzyl chloride
Carbon tetrachloride	1,2-Dichlorobenzene
cis-1,3-Dichloropropene	1,2,4-Trichlorobenzene
Benzene	Hexachlorobutadiene
1,2-Dichloroethane	
Trichloroethene	
1,2-Dichloropropane	
Toluene	
trans-1,3-Dichloropropene	

TABLE 6

REPLICATE PRECISION

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